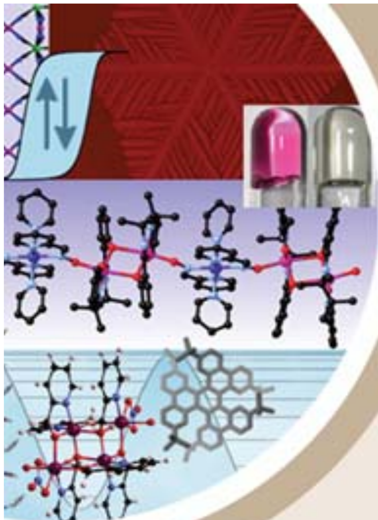
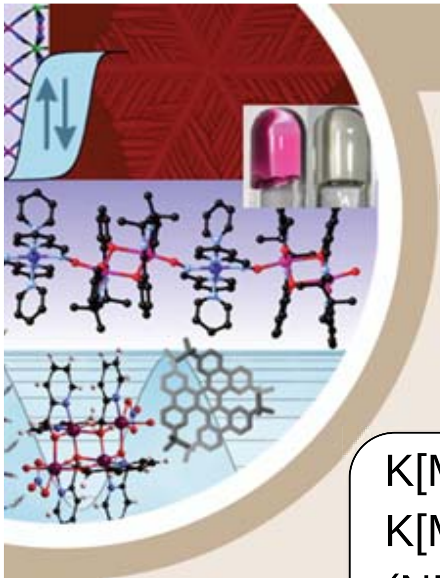


Introduction to SCMs

Dr. Rodolphe Clérac

CNRS - Researcher
Centre de Recherche Paul Pascal,
CNRS - UPR 8641
115, Avenue du Dr. A. Schweitzer
33600 Pessac – France
clerac@crpp-bordeaux.cnrs.fr

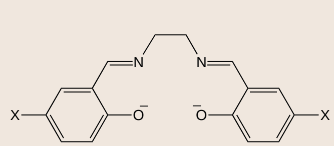


An example of Single-Chain Magnets

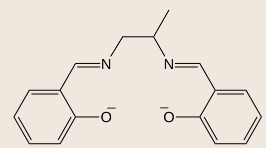
A real system made by design: a SMM building-block

$[Mn^{III}(salen)\text{-}Fe^{III}(CN)_6\text{-}Mn^{III}(salen)]$ trinuclear complexes:

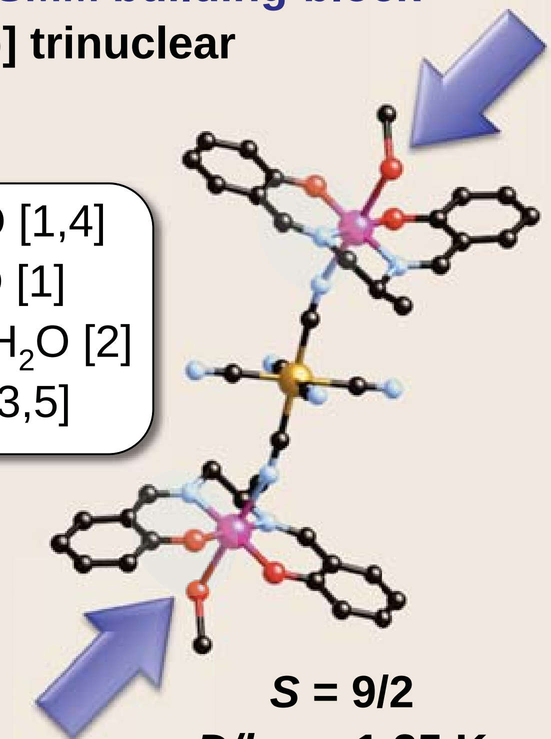
$K[Mn_2(5\text{-}Brsalen)_2(H_2O)_2Fe(CN)_6]\bullet 2H_2O$ [1,4]
$K[Mn_2(5\text{-}Clsalen)_2(H_2O)_2Fe(CN)_6]\bullet 2H_2O$ [1]
$(NEt_4)[Mn_2(5\text{-}Clsalen)_2(H_2O)_2Fe(CN)_6]\bullet H_2O$ [2]
$(NEt_4)[Mn_2(salmen)_2(MeOH)_2Fe(CN)_6]$ [3,5]



X = H: salen
X = Br: 5-Brsalen
X = Cl: 5-Clsalen

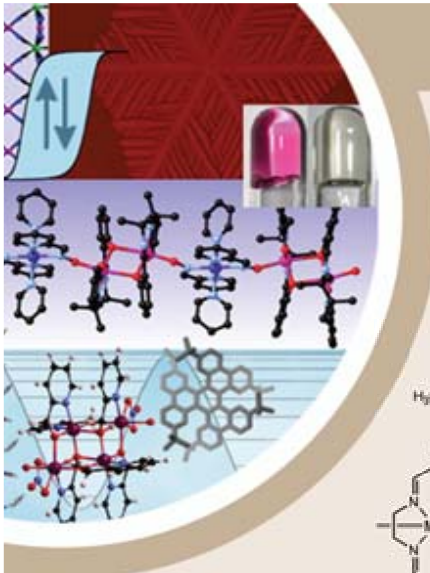


salmen



***S* = 9/2**
D/k_B = -1.25 K

[1] H. Miyasaka, N. Matsumoto, H. Okawa, N. Re, E. Gallo, C. Floriani *J. Am. Chem. Soc*. **1996**, *118*, 981
[2] H. Miyasaka, N. Matsumoto, N. Re, E. Gallo, C. Floriani *Inorg. Chem.* **1997**, *36*, 670
[3] H. Miyasaka, H. Ieda, N. Matsumoto, N. Re, E. Crescenzi, C. Floriani *Inorg. Chem.* **1998,** *37*, 255
[4] H. J. Choi, J. J. Sokol, J. R. Long *Inorg. Chem.* **2004**, *43*, 1606
[5] M. Ferbinteanu, H. Miyasaka, W. Wernsdorfer, K. Nakata, K. Sugiura, M. Yamashita, C. Coulon, R. Clérac, *J. Am. Chem. Soc.* **2005**, *127*, 3090

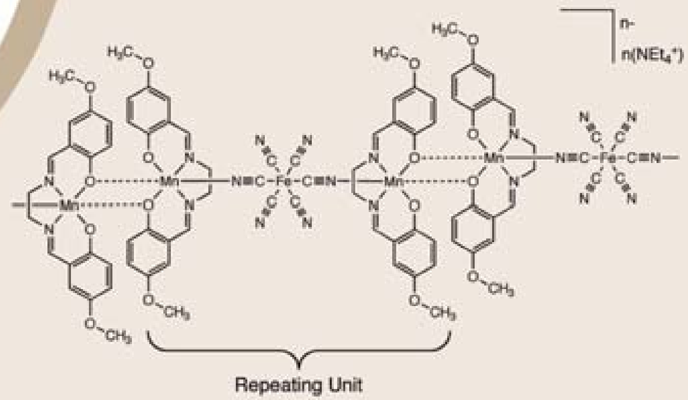


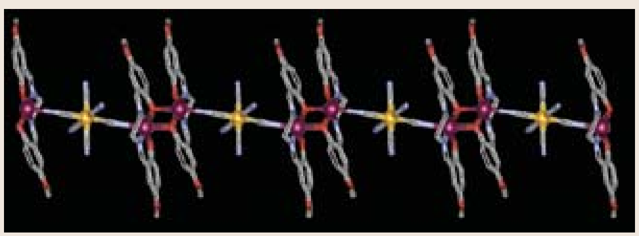
Single-Chain Magnets

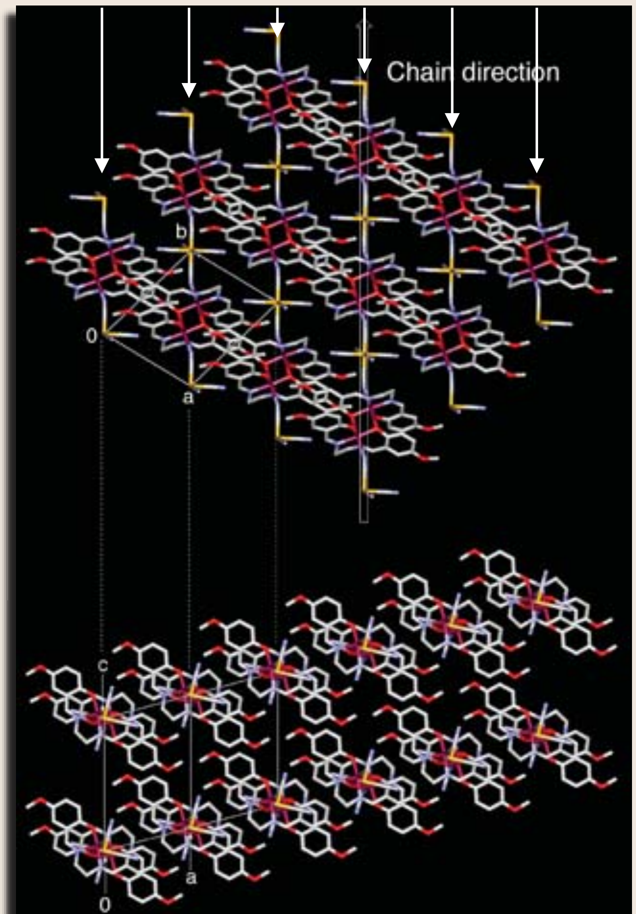
M. Ferbinteanu, H. Miyasaka, W. Wernsdorfer, K. Nakata, K. Sugiura, M. Yamashita, C. Coulon, R. Clérac, *J. Am. Chem. Soc.* **2005**, *127*, 3090

The structural arrangement:

$(NEt_4)_2[Mn(5\text{-}MeOsalen)]_2[Fe(CN)_6]$

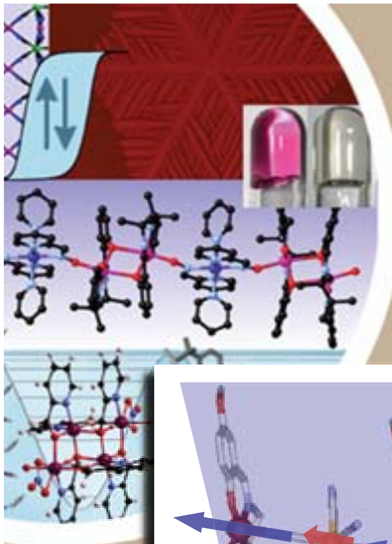






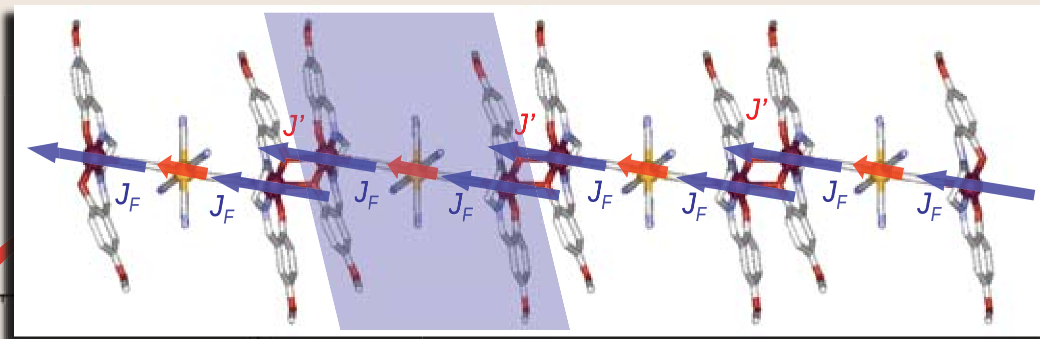
Isolated chains from a magnetic point of view

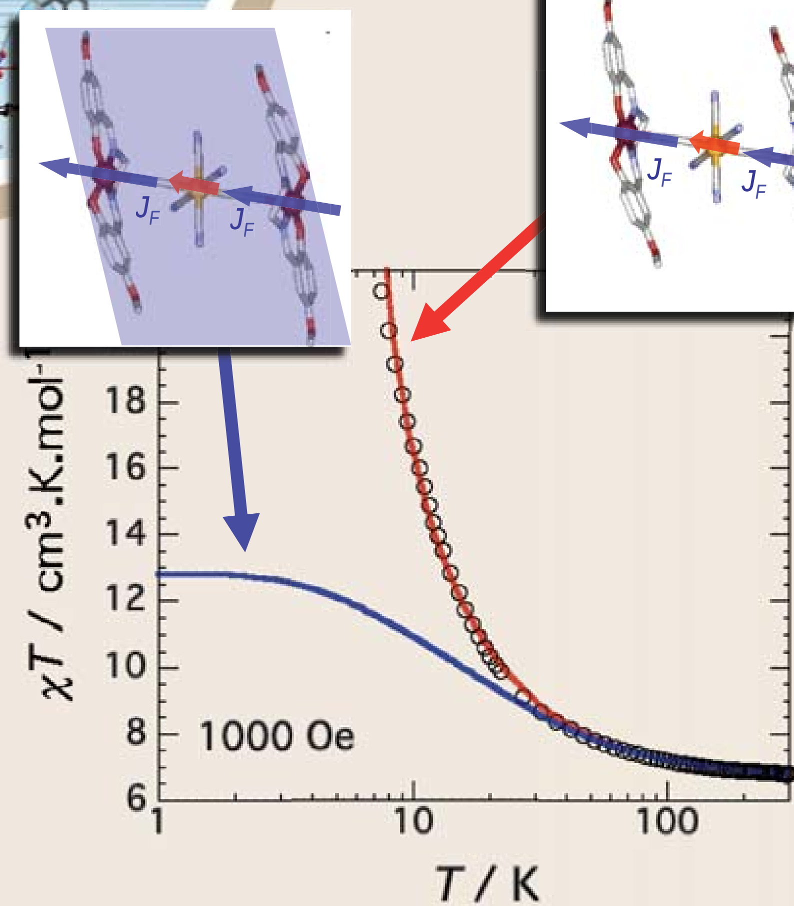
Single-Chain Magnets



The high temperature magnetic susceptibility:

$(NEt_4)_2[Mn(5\text{-}MeOsalen)]_2[Fe(CN)_6]$





with $H = -2J_F\left(\vec{S}_{Fe1}\vec{S}_{Mn} + \vec{S}_{Fe2}\vec{S}_{Mn}\right)$

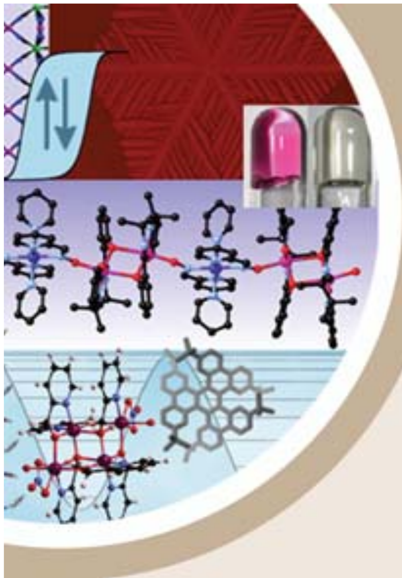
An Heisenberg trimer model

with inter-trimer *J'* interactions treated in a mean field approximation

J_F/k_B = +6.5(1) K

J'/k_B = +0.08(1) K

g = 2.03(2)



Single-Chain Magnets

A physicist view:

$(NEt_4)_2[Mn(5\text{-}MeOsalen)]_2[Fe(CN)_6]$

J_F/k_B = +6.5(1) K

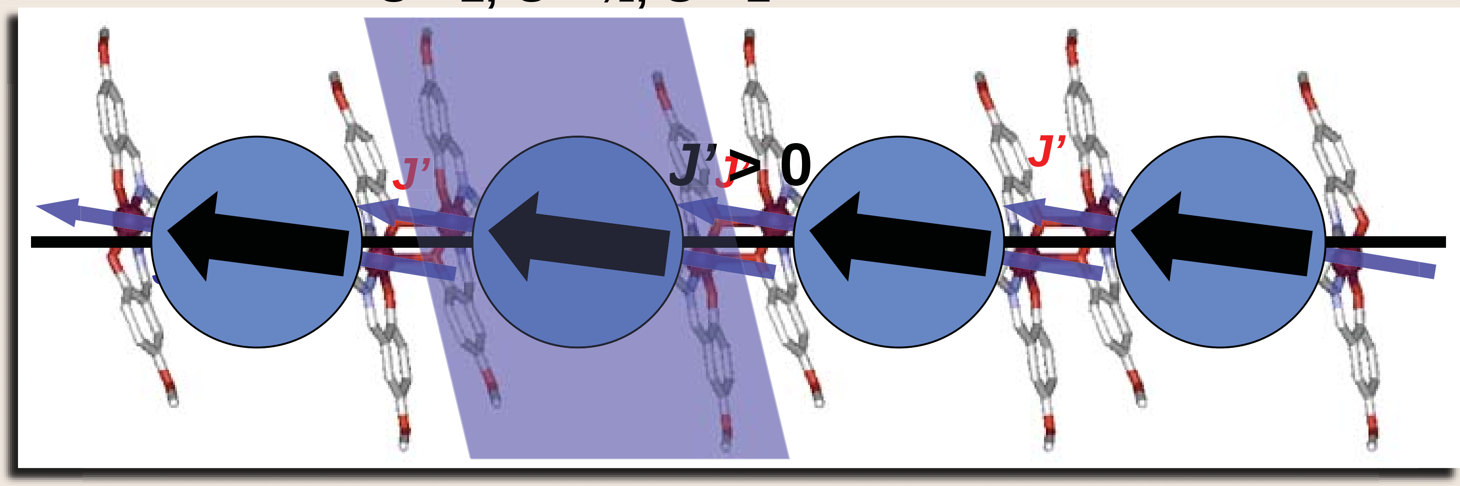
J'/k_B = +0.08(1) K

$J_{Mn\text{-}Mn}/k_B$ = +0.40(6) K

« S_T = 9/2 »

S = 2, S = ½, S = 2

because $|J_F| \gg J_{Mn\text{-}Mn}$ and for $|J_F| \gg k_BT$

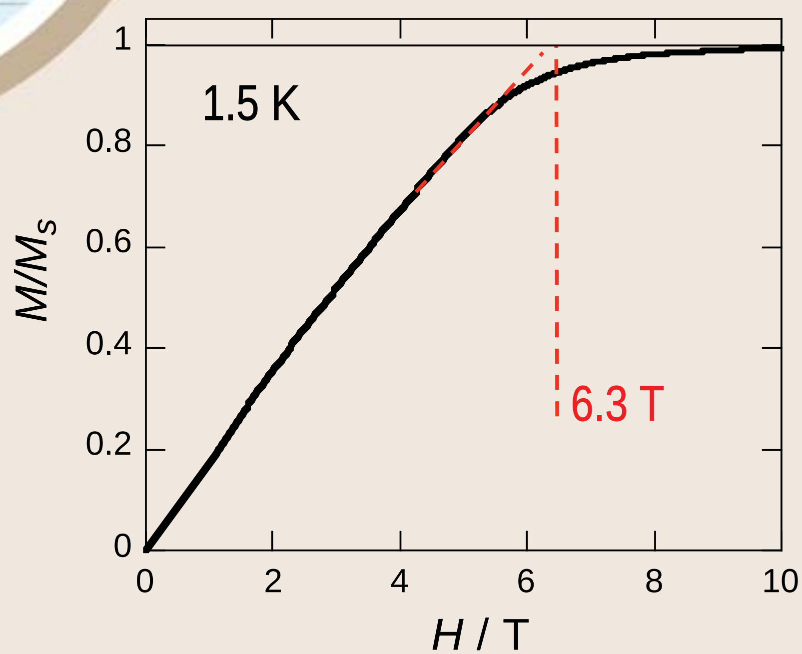


Chain of ferromagnetically coupled anisotropic *S* = 9/2 spins
(it is fundamental to prove that the system is 1-D)

Single-Chain Magnets

Single crystal measurements: *H* in the hard plane

$(NEt_4)_2[Mn(5\text{-}MeOsalen)]_2[Fe(CN)_6]$

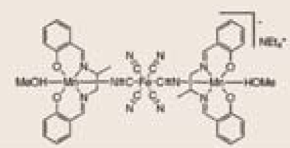


$$H = -2J'\sum_{-\infty}^{+\infty}\vec{S}_{T,i}\vec{S}_{T,i+1} + D\sum_{-\infty}^{+\infty}\vec{S}^{2}_{T,iz}$$

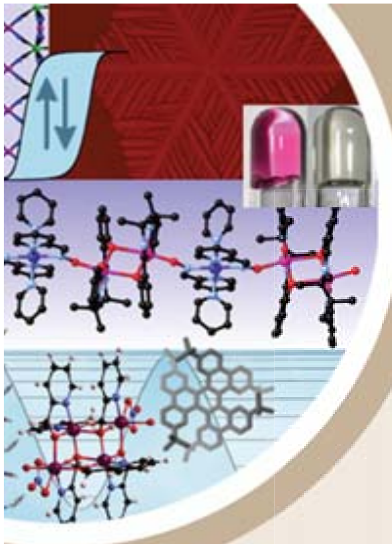
Estimation of *D*

$$2DS_T^2 \approx g\mu_B S_T H_a$$

D/k_B = -0.94 K



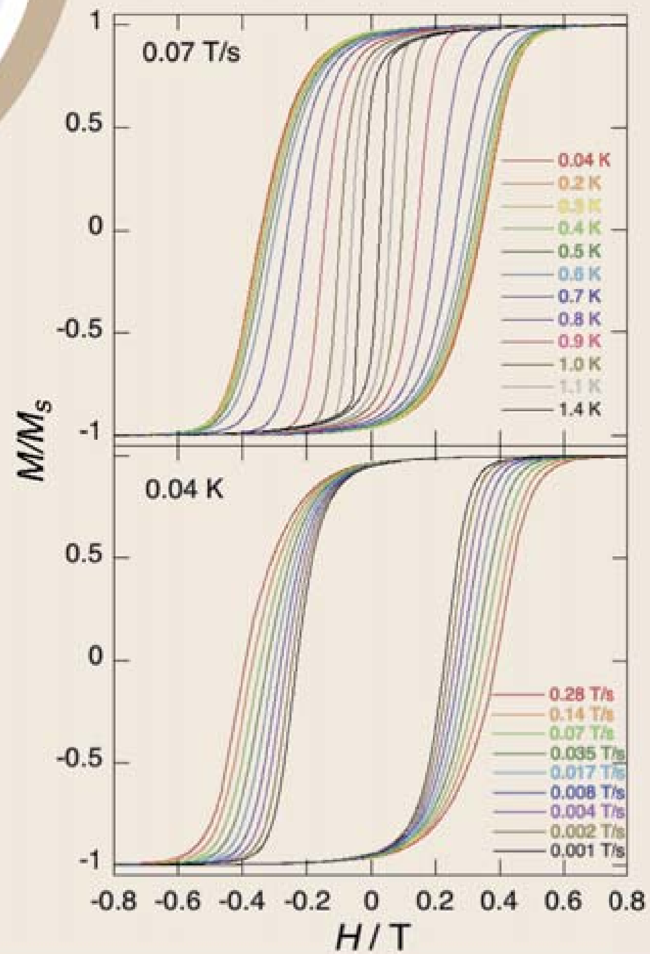
$D/k_B \approx$ -1.25 K



Single-Chain Magnets

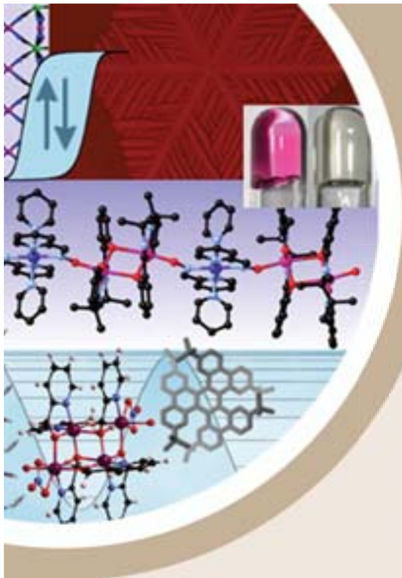
Single crystal measurements: *H* along the easy axis

$(NEt_4)_2[Mn(5\text{-}MeOsalen)]_2[Fe(CN)_6]$



M vs *H*
hysteresis loops

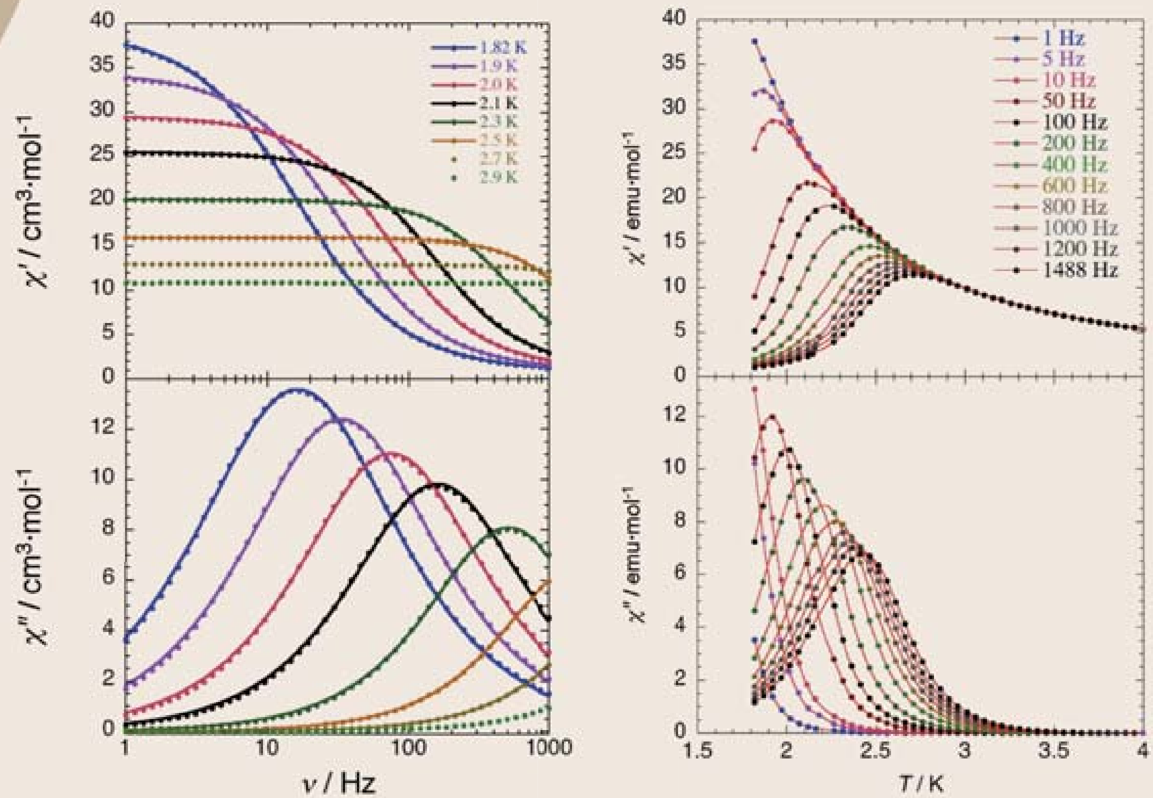
Magnet behavior, i.e. slow relaxation of the magnetization compatible with SCM behavior



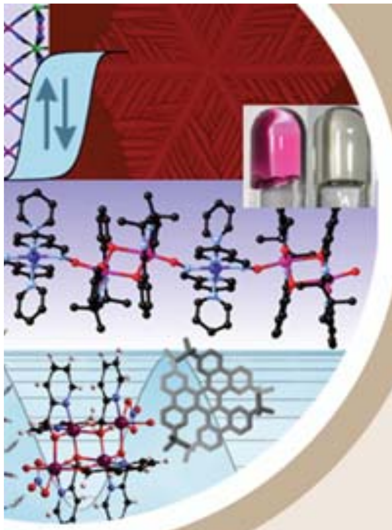
Single-Chain Magnets

Relaxation time measurements (ac susceptibility):

$(NEt_4)_2[Mn(5\text{-}MeOsalen)]_2[Fe(CN)_6]$



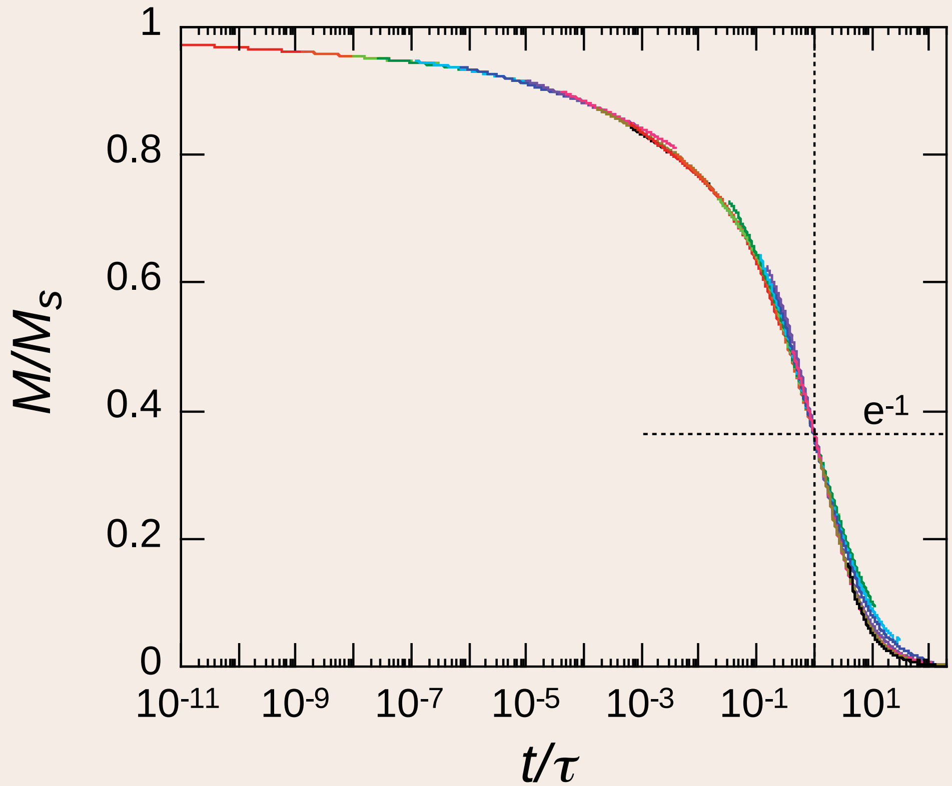
A single relaxation mode compatible with SCM behavior



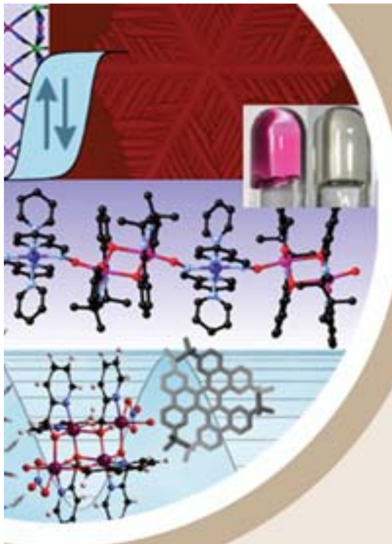
Single-Chain Magnets

Relaxation time measurements (*M* vs time):

$(NEt_4)_2[Mn(5\text{-}MeOsalen)]_2[Fe(CN)_6]$



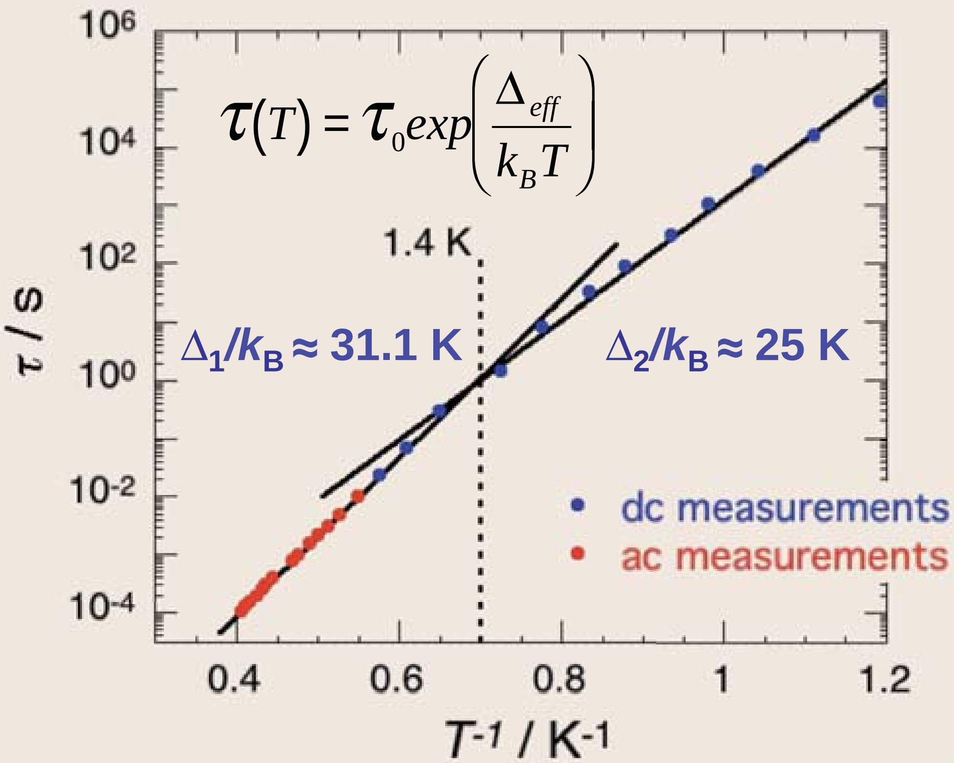
Determination of the relaxation time down to 0.8 K



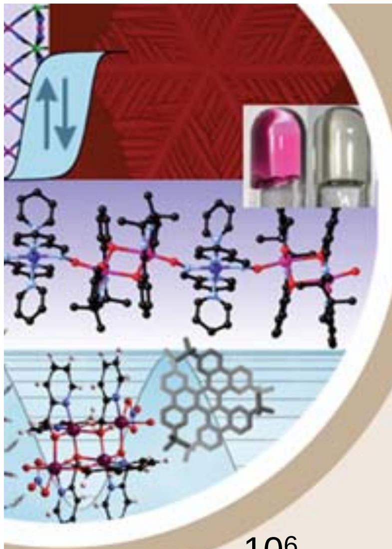
Single-Chain Magnets

Relaxation time:

$(NEt_4)_2[Mn(5\text{-}MeOsalen)]_2[Fe(CN)_6]$



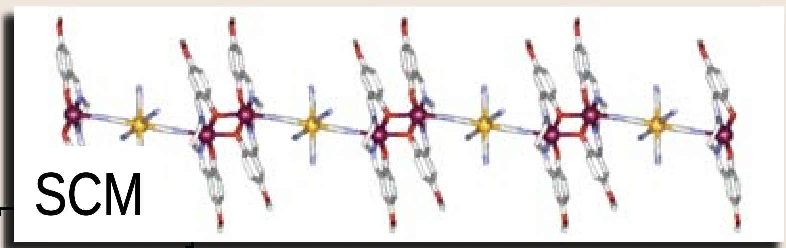
Crossover between two activated relaxation regimes

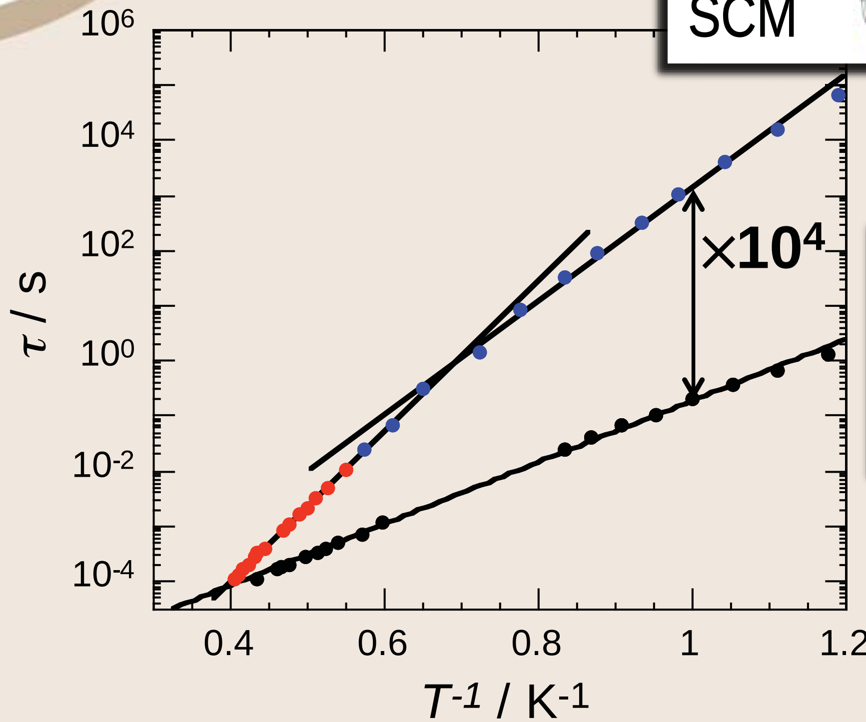


Single-Molecule vs. Single-Chain Magnets

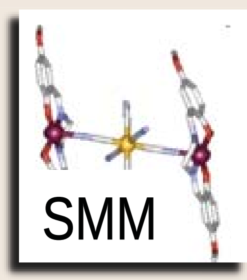
Relaxation time SMM vs SCM:

$(NEt_4)_2[Mn(5\text{-}MeOsalen)]_2[Fe(CN)_6]$

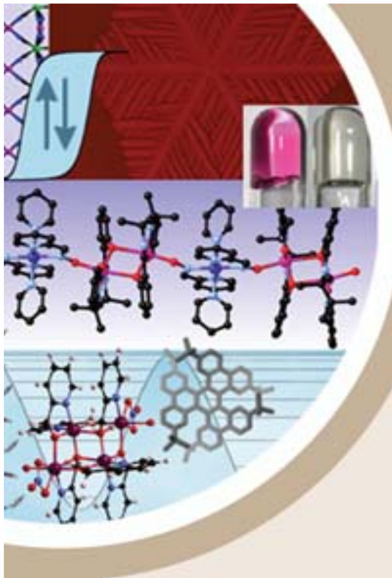




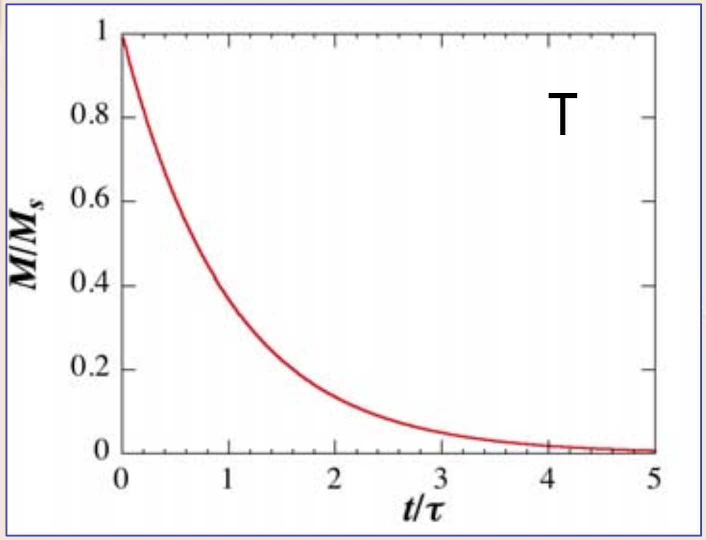
(NEt_4)
$[Mn(salmen)(MeOH)]_2[Fe(CN)_6]$



In a given temperature range the correlations enhance the relaxation time

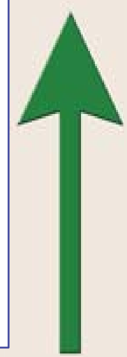


Chain of Ising spins

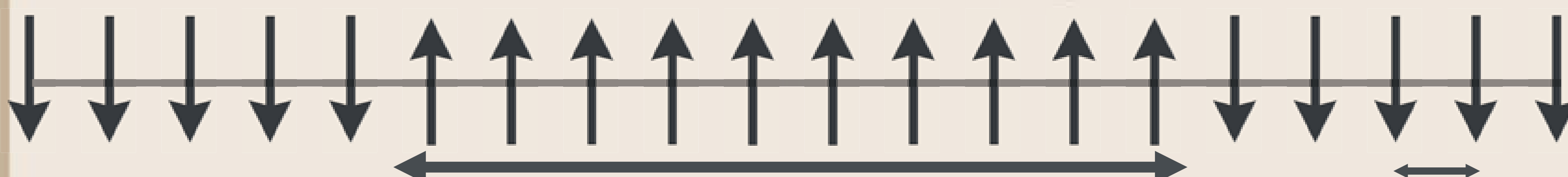


(a) Glauber, R. J. *J. Math. Phys.* **1963**, *4*, 294; (b) Coulon, C. ; Miyasaka, H. ; Clérac, R. *Struct. Bond.* **2006**, *122*, 163

$$M / M_S = exp\left(-\frac{t}{\tau}\right)$$



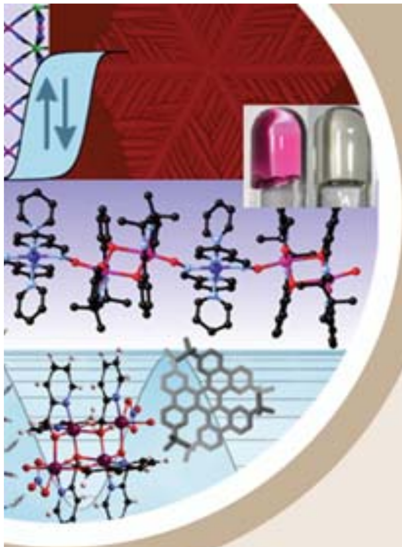
H ≠ 0



$$H = -2J'S^2 \sum_{-\infty}^{+\infty} \vec{\sigma}_i \vec{\sigma}_{i+1}$$

$$\tau(T) = \tau_i(T)\left(\frac{\xi}{a}\right)^2 = \tau_i(T) exp\left(\frac{2\Delta_\xi}{k_B T}\right)$$

with $\Delta_\xi = 4J'S^2$



Real Single-Chain Magnets

The relaxation time of a Single-Chain Magnet: Chain of ferromagnetically coupled Ising spins (Glauber)

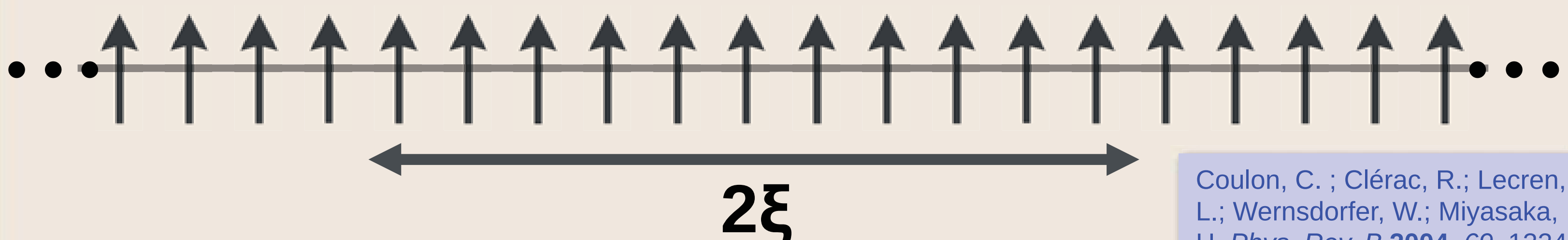
$$\tau(T) = \tau_i(T) exp\left(\frac{2\Delta_\xi}{k_B T}\right) \text{ with } \Delta_\xi = 4J'S^2$$

(a) Glauber, R. J. *J. Math. Phys.* **1963**, *4*, 294; (b) Coulon, C. ; Miyasaka, H. ; Clérac, R. *Struct. Bond.* **2006**, *122*, 163

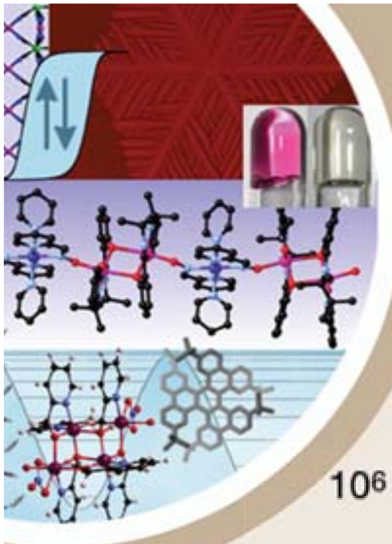
1) For a chain of anisotropic spins (*D* < 0 and |*D/J* | > 4/3: Ising limit) :

$$H = -2J' \sum_{-\infty}^{+\infty} \vec{S}_{T,i} \vec{S}_{T,i+1} + D \sum_{-\infty}^{+\infty} \vec{S}^2_{T,iz}$$

$$\tau_i(T) = \tau_0 exp\left(\frac{\Delta_A}{k_B T}\right) \text{ with } \Delta_A = |D| S_T^2 \quad \Rightarrow \quad \tau(T) = \tau_0 exp\left(\frac{2\Delta_\xi + \Delta_A}{k_B T}\right)$$



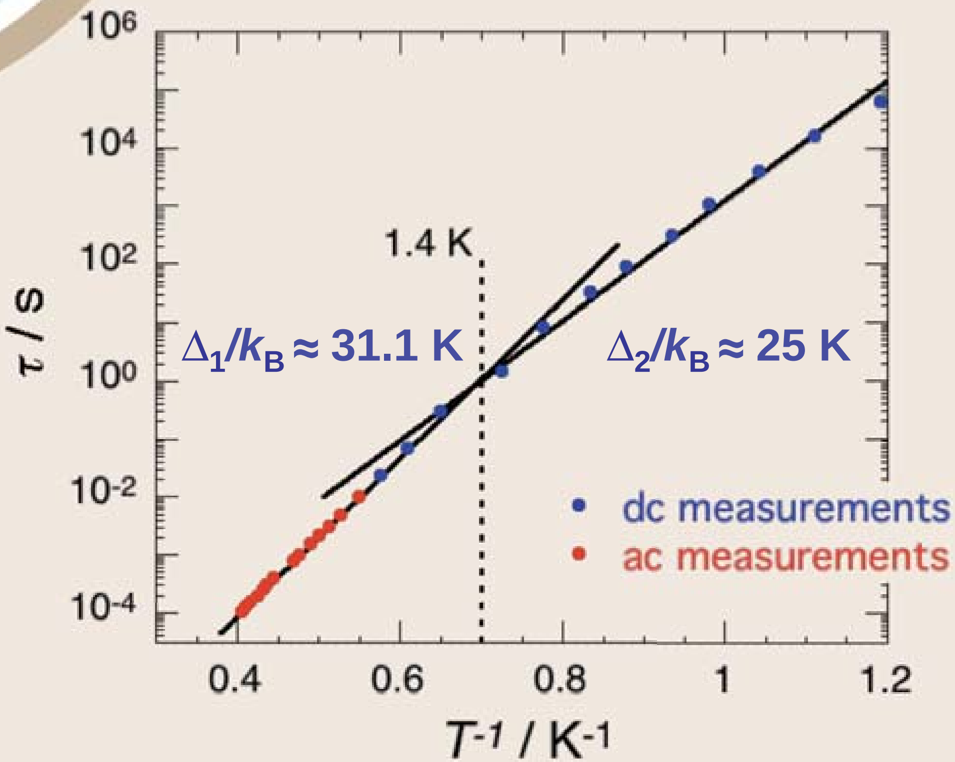
Coulon, C. ; Clérac, R.; Lecren, L.; Wernsdorfer, W.; Miyasaka, H. *Phys. Rev. B* **2004**, *69*, 132408



Single-Chain Magnets

Relaxation time: the Glauber's regime

$(NEt_4)_2[Mn(5\text{-}MeOsalen)]_2[Fe(CN)_6]$



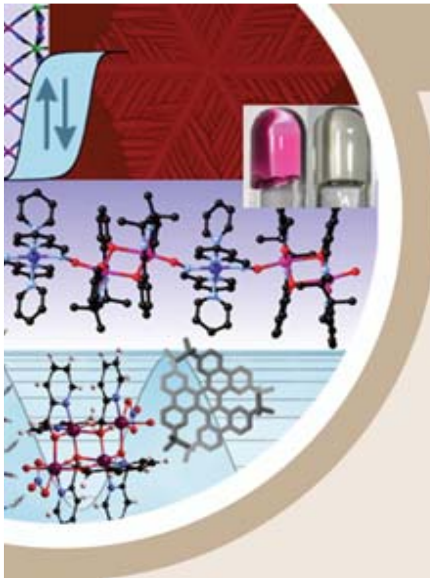
with $S_T = 9/2$
$J'/k_B \approx 0.08$ K
$D/k_B = -0.94$ K
$(|D/J'| >> 4/3)$

$$\tau(T) = \tau_0 exp\left(\frac{2\Delta_\xi + \Delta_A}{k_B T}\right)$$

with

$$2\Delta_\xi + \Delta_A = 8J'S_T^2 + |D|S_T^2$$

$\Delta_1/k_B = (8J' + |D|)S_T^2/k_B$
$= 32$ K



Single-Chain Magnets

The relaxation time in a Single-Chain Magnet:

2) For a chain of anisotropic spins with a length *L*
(*D* < 0 and |*D/J* | > 4/3 Ising limit):

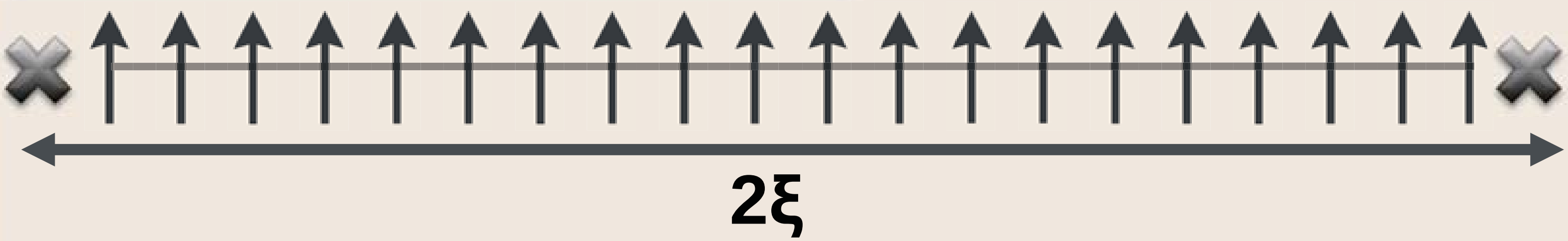
(a) Coulon, C. ; Miyasaka, H. ; Clérac, R. *Struct. Bond.* **2006**, *122*, 163
(b) Coulon, C. ; Clérac, R.; Lecren, L.; Wernsdorfer, W.; Miyasaka, H. *Phys. Rev. B* **2004**, *69*, 132408

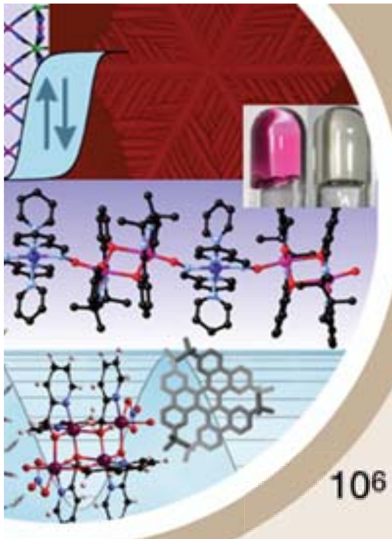
$$H = -2J'\sum_{-\infty}^{+\infty} \vec{S}_{T,i}\vec{S}_{T,i+1} + D\sum_{-\infty}^{+\infty} \vec{S}_{T,iz}^{2}$$

for $2\xi < L$ $\quad\Rightarrow\quad \tau(T) = \tau_0 exp\left(\dfrac{2\Delta_\xi + \Delta_A}{k_B T}\right)$

for $2\xi > L$ $\quad\Rightarrow\quad \tau(T) = \tau_0 exp\left(\dfrac{\Delta_\xi + \Delta_A}{k_B T}\right)$

Luscombe, J. H. et al., *Phys. Rev. E* **1996**, *53*, 5852
Leal da Silva, J. K. et al., *Phys. Rev. E* **1995**, *52*, 4527

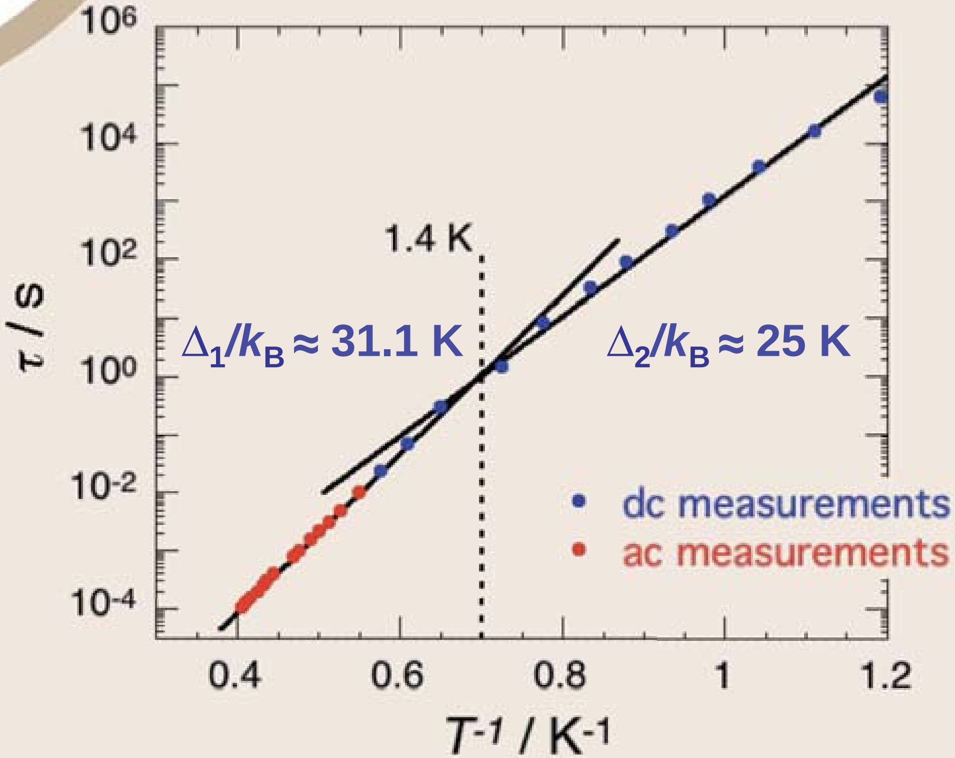




Single-Chain Magnets

Relaxation time: the finite-size chain regime

$(NEt_4)_2[Mn(5\text{-}MeOsalen)]_2[Fe(CN)_6]$



with S_T = 9/2

$J'/k_B \approx 0.08$ K

D/k_B = -0.94 K

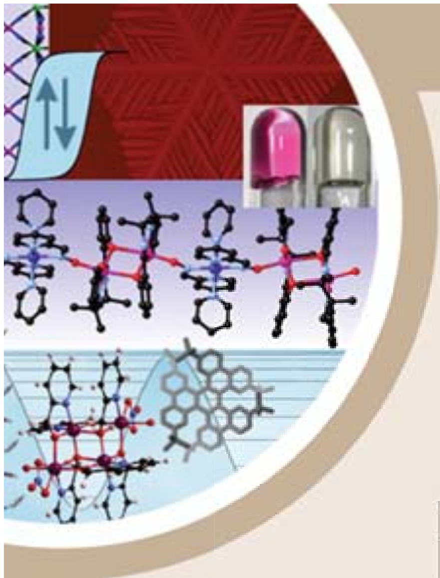
($|D/J'| >> 4/3$)

$$\tau(T) = \tau_0 exp\left(\frac{\Delta_\xi + \Delta_A}{k_B T}\right)$$

with

$$\Delta_\xi + \Delta_A = 4J'S_T^2 + |D|S_T^2$$

$\Delta_2/k_B = (4J' + |D|)S_T^2/k_B$
= 25.5 K

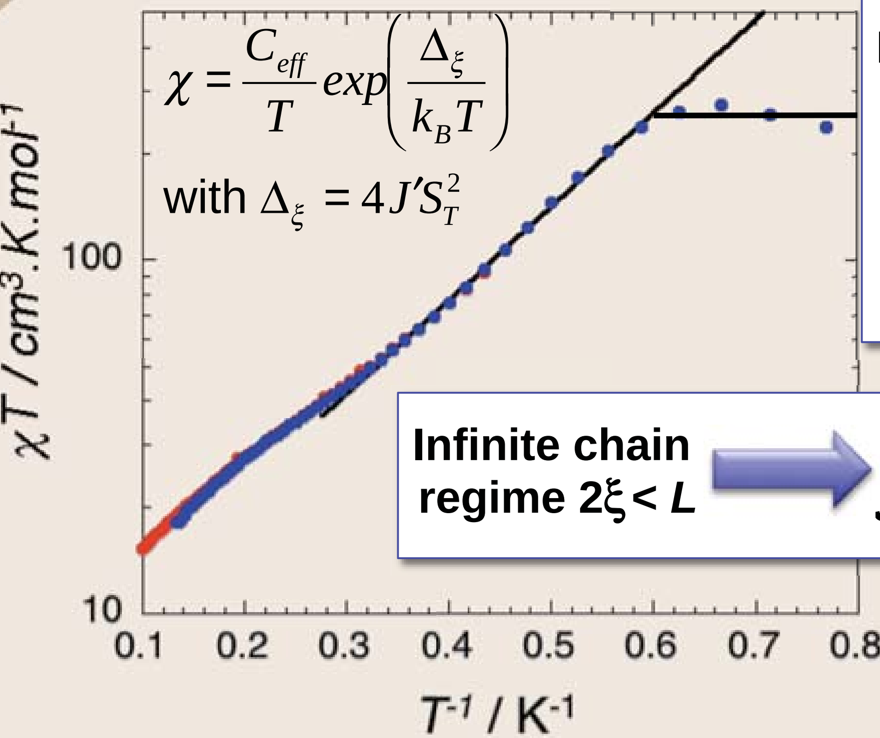


Final proof of a Single-Chain Magnets

Another evidence of the finite-size chain regime:

$(NEt_4)_2[Mn(5\text{-}MeOsalen)]_2[Fe(CN)_6]$

Ising Chain Model $H = -2J' S_T^2 \sum_{-\infty}^{+\infty} \vec{\sigma}_i \vec{\sigma}_{i+1}$



Finite chain regime $2\xi > L$

$\chi = n \frac{C_{eff}}{T}$

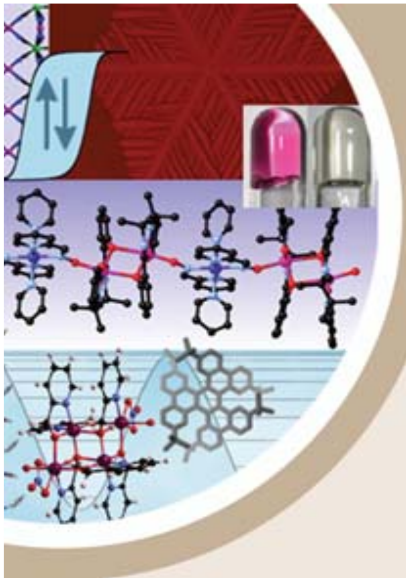
***n* ≈ 44**

***L* ≈ 60 nm**

Infinite chain regime $2\xi < L$

$S_T = 9/2$

$J'/k_B = +0.08(1)$ K



Single-Chain Magnets (Take home message)

$$H = -2J'\sum_{-\infty}^{+\infty}\vec{S}_{T,i}\vec{S}_{T,i+1} + D\sum_{-\infty}^{+\infty}\vec{S}_{T,iz}^{2}$$

(a) Coulon, C.; Miyasaka, H. ; Clérac, R. *Struct. Bond.* **2006**, *122*, 163
(b) Coulon, C.; Clérac, R.; Lecren, L.; Wernsdorfer, W.; Miyasaka, H. *Phys. Rev. B* **2004**, *69*, 132408

Always correct:

Static properties $\chi = \frac{C_{eff}}{T} exp\left(\frac{\Delta_\xi}{k_B T}\right)$

Dynamic properties

for $2\xi < L$ ⇒ $\tau(T) = \tau_0 exp\left(\frac{2\Delta_\xi + \Delta_A}{k_B T}\right)$

for $2\xi > L$ ⇒ $\tau(T) = \tau_0 exp\left(\frac{\Delta_\xi + \Delta_A}{k_B T}\right)$

In the Ising limit *D* < 0 and |*D/J* | > 4/3: $\Delta_\xi = 4J'S_T^2$ and $\Delta_A = |D|S_T^2$

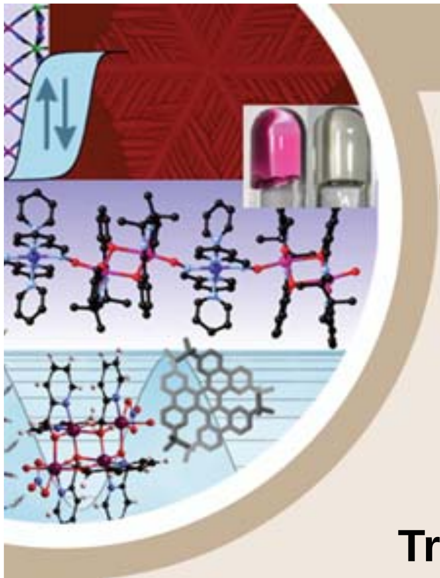
In the Heisenberg limit *D* < 0, and small and |*D/J* | << 4/3:

$$\Delta_\xi = 2S_T^2\sqrt{2|DJ'|} \text{ and } \Delta_A = ??$$

Between the Ising and the Heisenberg limits (*D* < 0, |*D/J* | < 4/3):

$$\Delta_\xi = ?? \text{ and } \Delta_A = ??$$

Billoni, O. V.; Pianet, V.; Pescia, D.; Vindigni, A. *Phys. Rev. B* **2011**, *84*, 064415



Single-Chain Magnets recipe

The ingredients in order to obtain a SCM:

- **chain architecture**
- **high-spin chain units with uniaxial anisotropy**
- **large intra-chain magnetic interaction**
- **as small as possible inter-chain interactions**

Transition metals organized by ligands:

- 3d: Mn(III), Fe(III), Ni(II), Co(II), V(II)
- Lanthanides: Tb(III), Dy(III), Ho(III)
- Mixed metals 3d/3d or 4f/4f or 3d/4f
- Mixed spins: 3d/radical and 4f/radical

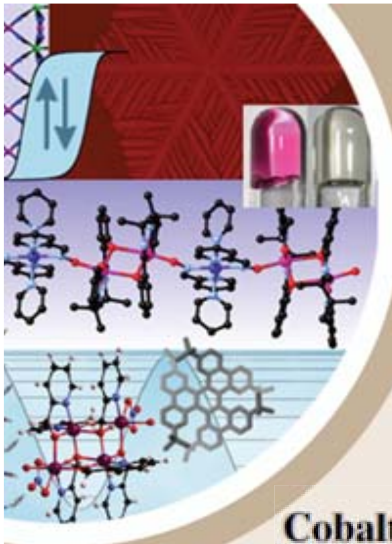
Polynuclear complexes organized by linkers:

- SMMs
- anisotropic complexes

Synthesis methods:

- serendipitous!
- by design

➡ **There are a few SCM examples in the literature since 2001**

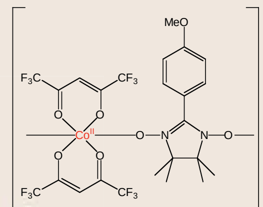


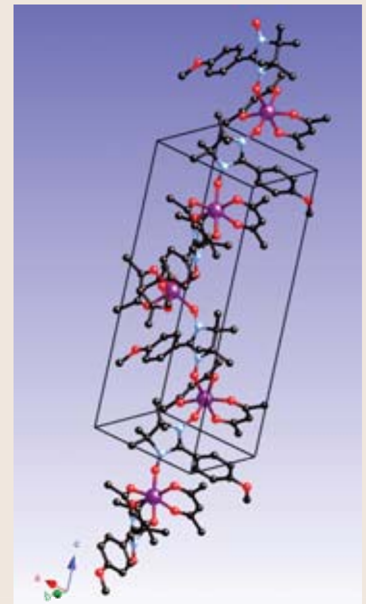
Single-Chain Magnets

The first chain exhibiting slow relaxation:

$Co^{II}(hfac)_2(NITPhOMe)$

hfac: hexafluoroacetylacetonate
NITPhOMe: 4'-methoxy-phenyl-4,4,5,5-tetramethyl imidazoline-1-oxyl-3-oxide

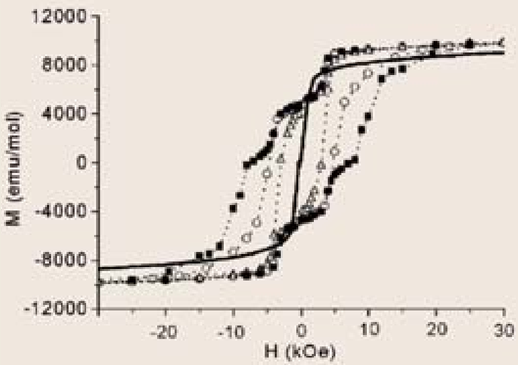


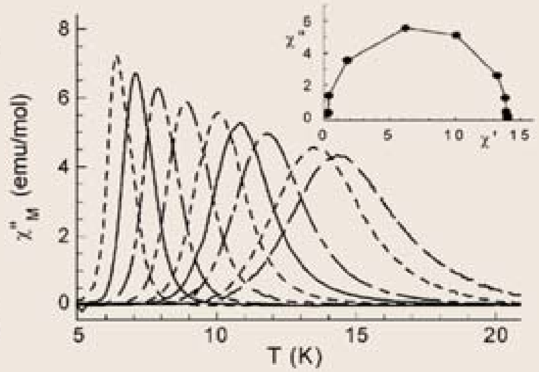


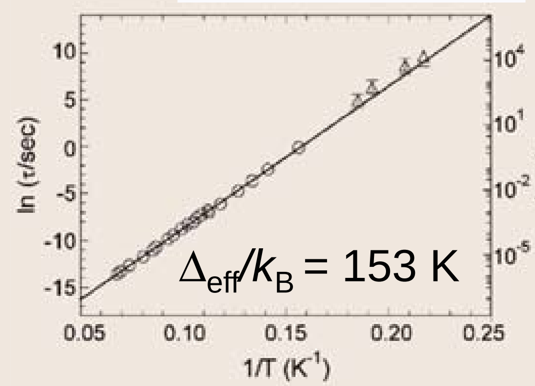
Cobalt(II)-Nitronyl Nitroxide Chains as Molecular Magnetic Nanowires

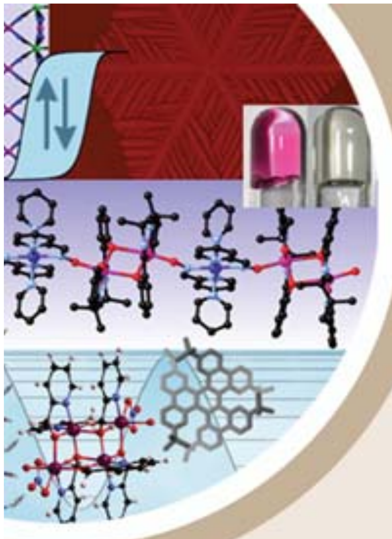
Andrea Caneschi, Dante Gatteschi,* Nikolia Lalioti, Claudio Sangregorio, Roberta Sessoli, Giovanni Venturi, Alessandro Vindigni, Angelo Rettori, Maria G. Pini, and Miguel A. Novak

Angew. Chem. Int. Ed. **2001,** *40*, 1760









Single-Chain Magnets

The first Single-Chain Magnet:

$[Mn_2(saltmen)_2Ni(pao)_2(py)_2](ClO_4)_2$

$saltmen^{2-}$: N,N'–(1,1,2,2-tetramethylethylene) bis(salicylideneiminate)
pao^{-}: pyridine-2-aldoximate; py: pyridine

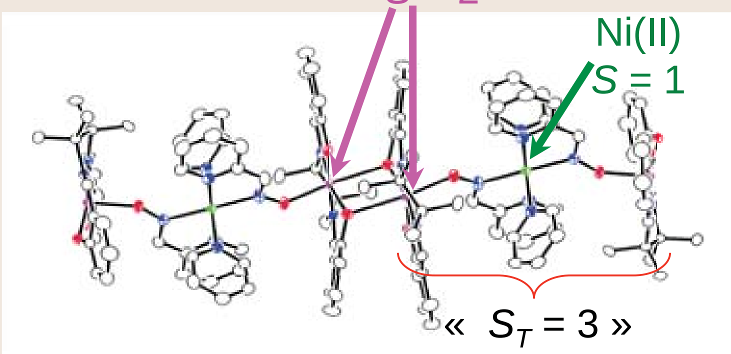
Evidence for Single-Chain Magnet Behavior in a Mn^{III}–Ni^{II} Chain Designed with High Spin Magnetic Units: A Route to High Temperature Metastable Magnets

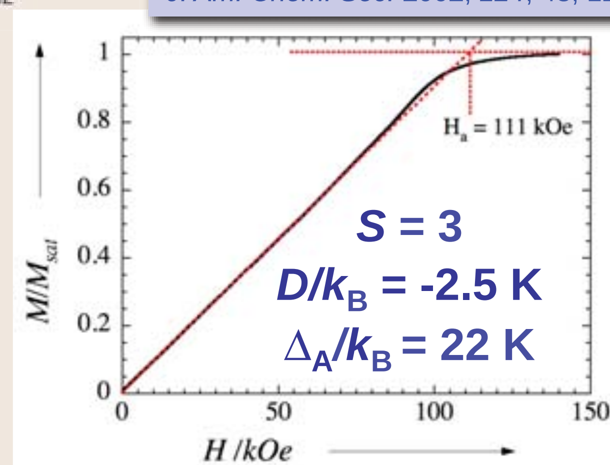
Rodolphe Clérac,*,† Hitoshi Miyasaka,*,‡,§ Masahiro Yamashita,‡ and Claude Coulon†

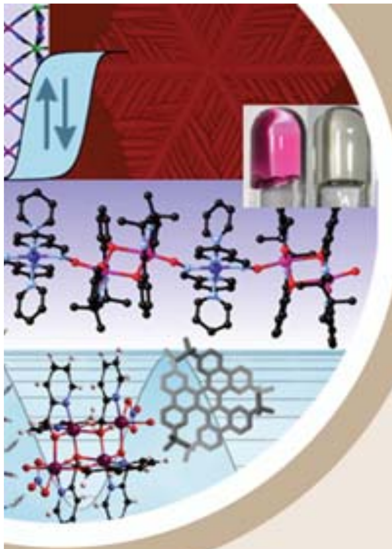
Contribution from the Centre de Recherche Paul Pascal, CNRS UPR 8641, avenue du Dr. A. Schweitzer, 33600 Pessac, France, and "Structural Ordering and Physical Properties", PRESTO, Japan Science and Technology Corporation (JST) and Department of Chemistry, Graduate School of Science, Tokyo Metropolitan University, Minami-Ohsawa 1-1, Hachioji, Tokyo 192-0397, Japan

Received February 28, 2002

J. Am. Chem. Soc. **2002**, *124*, 43, 12837





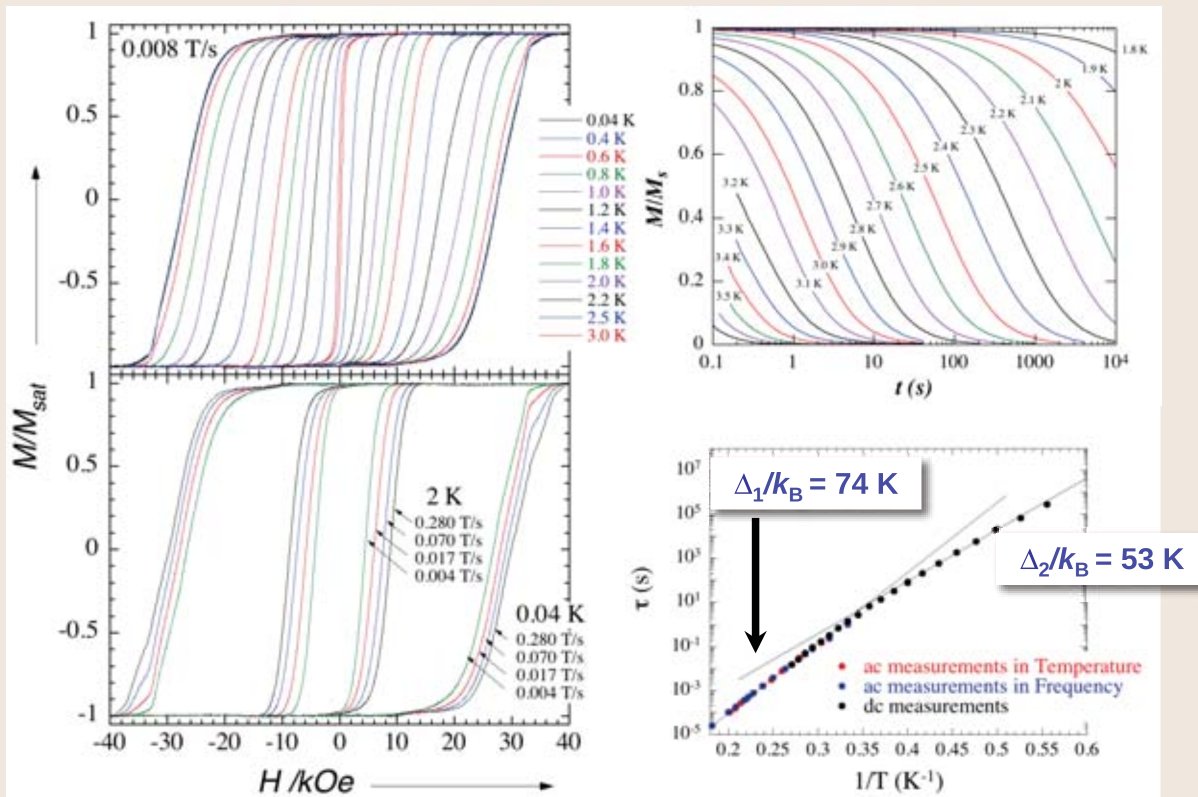


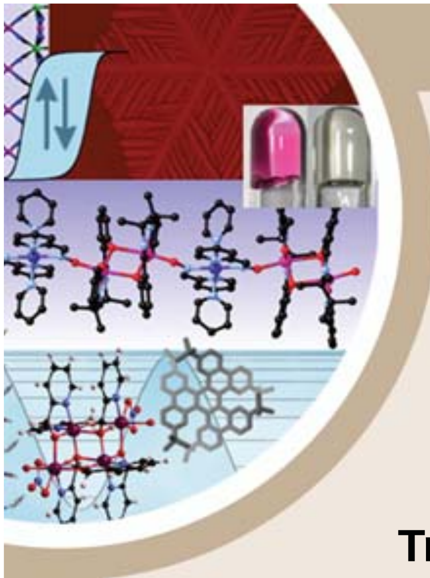
Single-Chain Magnets

The Single-Chain Magnet:
$[Mn_2(saltmen)_2Ni(pao)_2(py)_2](ClO_4)_2$

$\Delta_A/k_B = 22$ K
$\Delta_\xi/k_B = 28$ K

$\Delta_{1,theo}/k_B = 78$ K
$\Delta_{2,theo}/k_B = 50$ K





Single-Chain Magnets recipe

The ingredients in order to obtain a SCM:

- **chain architecture**
- **high-spin chain units with uniaxial anisotropy**
- **large intra-chain magnetic interaction**
- **as small as possible inter-chain interactions**

Transition metals organized by ligands:

- 3d: Mn(III), Fe(III), Ni(II), Co(II), V(II)
- Lanthanides: Tb(III), Dy(III), Ho(III)
- Mixed metals 3d/3d or 4f/4f or 3d/4f
- Mixed spins: 3d/radical and 4f/radical

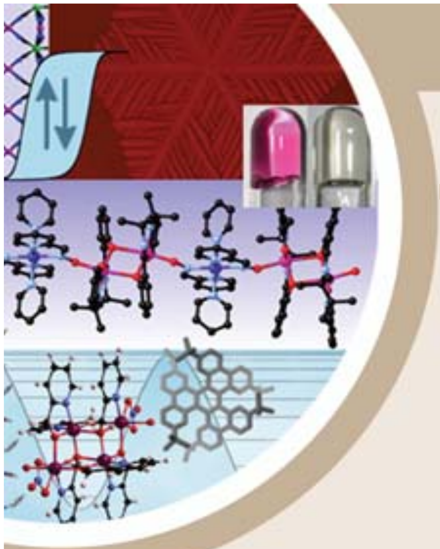
Polynuclear complexes organized by linkers:

- SMMs
- anisotropic complexes

Synthesis methods:

- serendipitous
- by design

➡ **There are a few SCM examples in the literature since 2001**

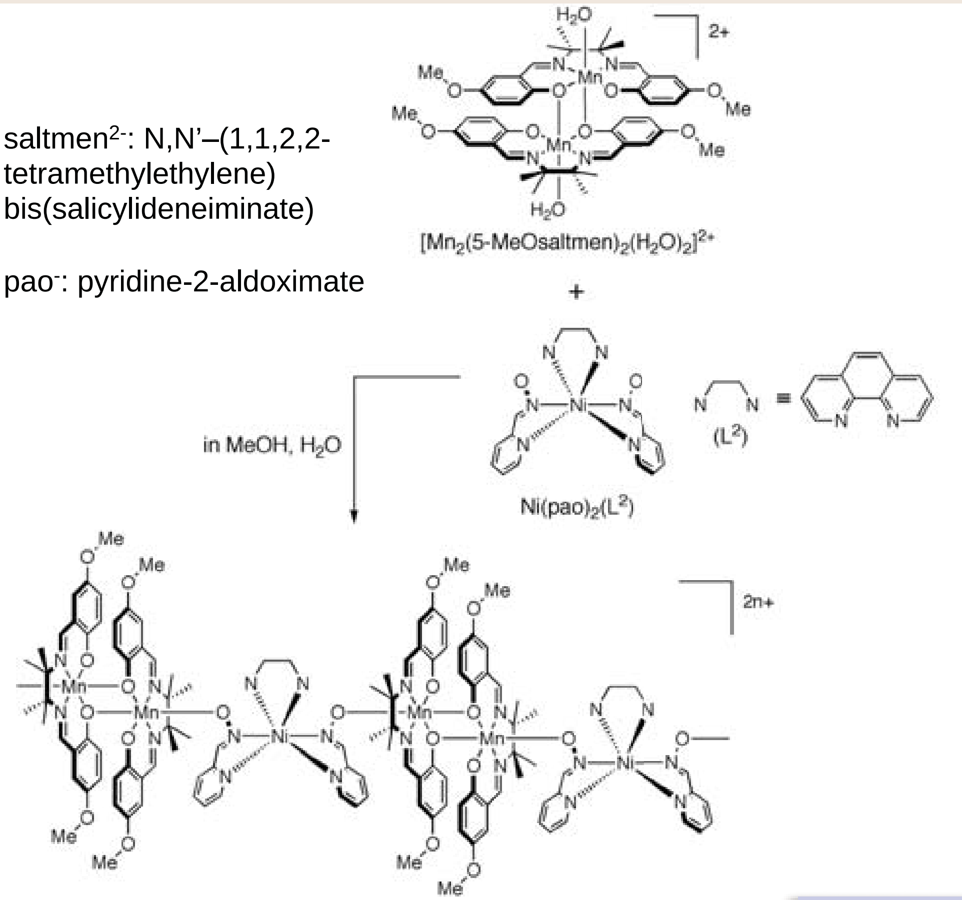


Single-Chain Magnets

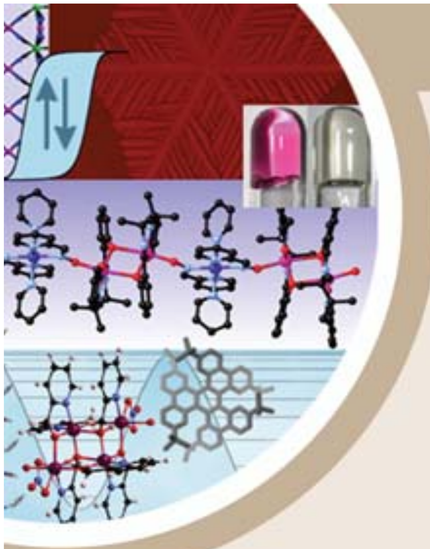
The synthesis: $[Mn_2(5\text{-}MeOsaltmen)_2Ni(pao)_2(phen)_2](ClO_4)_2$

saltmen^{2-}: N,N'–(1,1,2,2-tetramethylethylene) bis(salicylideneiminate)

pao^{-}: pyridine-2-aldoximate

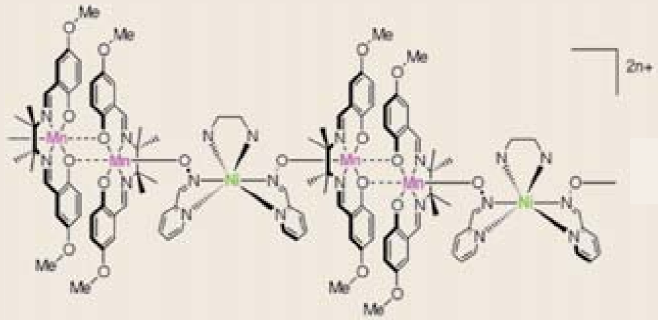


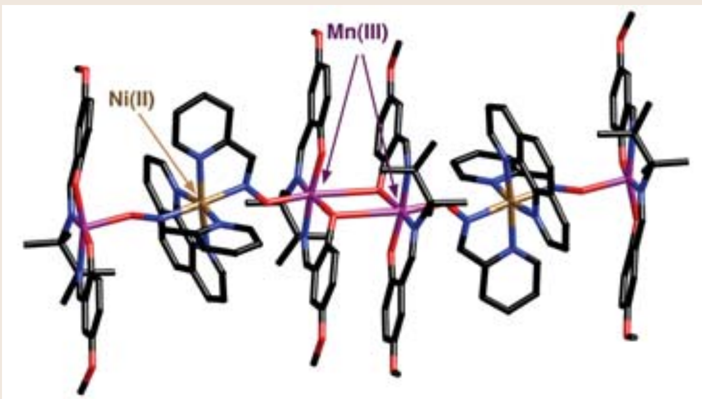
Phys. Rev. Lett. **2009** *102*, 167204

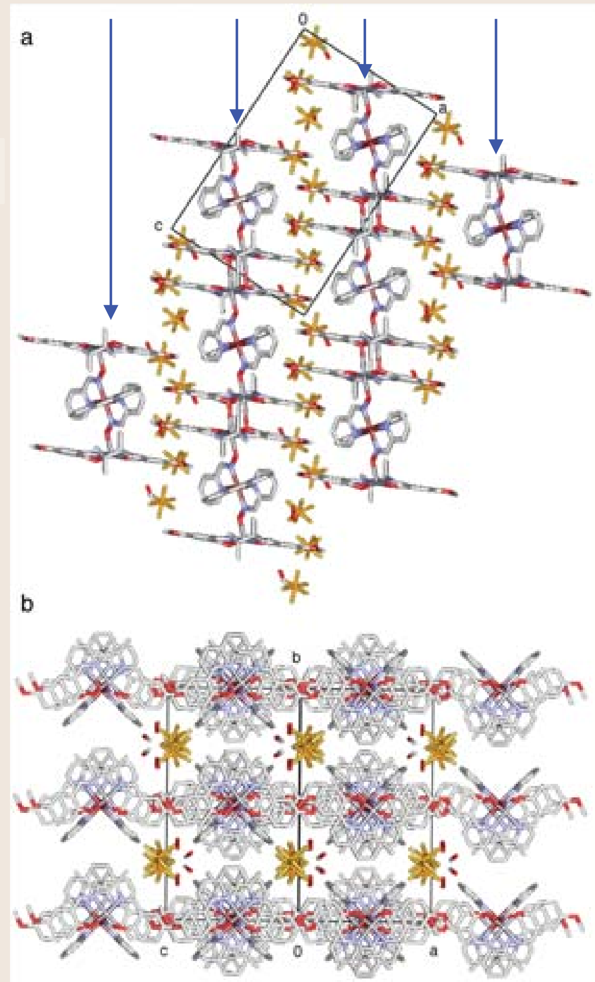


Single-Chain Magnets

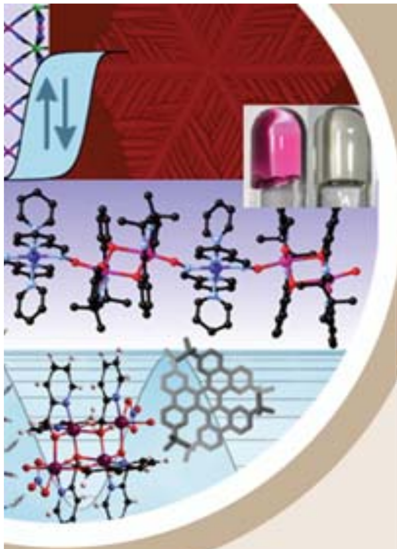
$[Mn_2(5\text{-}MeOsaltmen)_2Ni(pao)_2(phen)_2](ClO_4)_2$





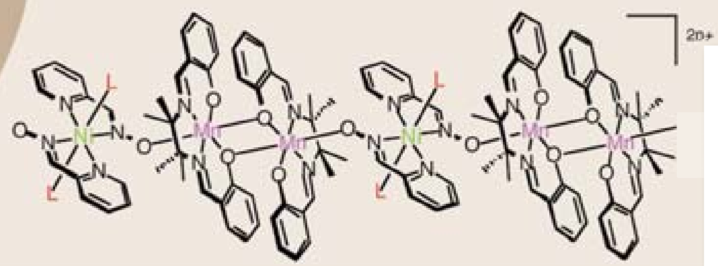


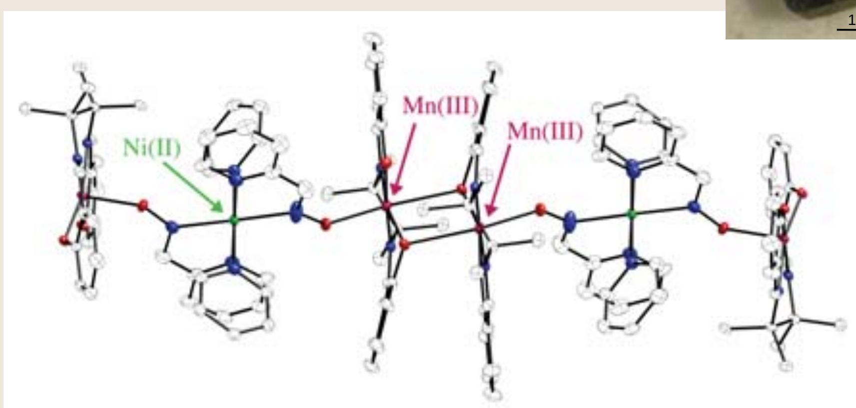
***Phys. Rev. Lett.* 2009** *102*, 167204

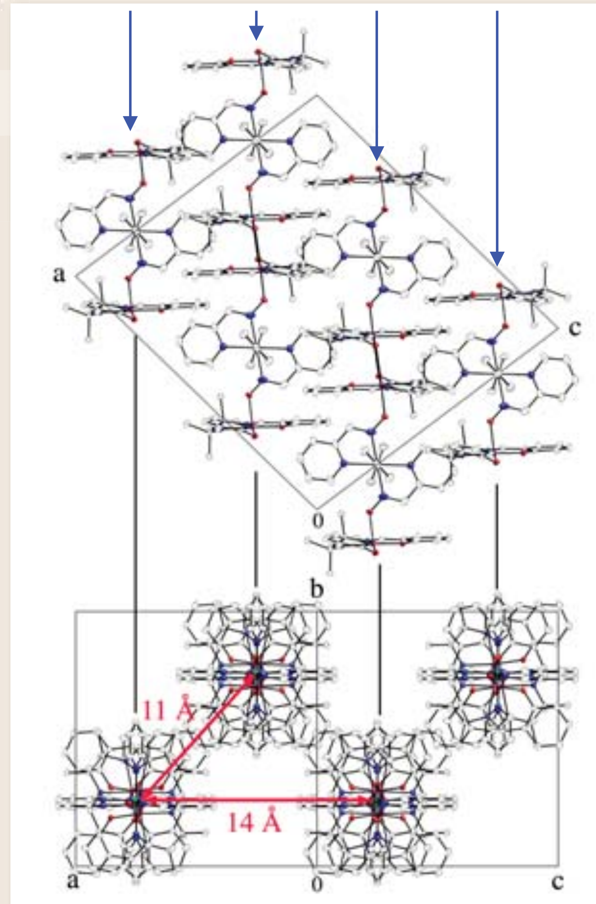


Single-Chain Magnets

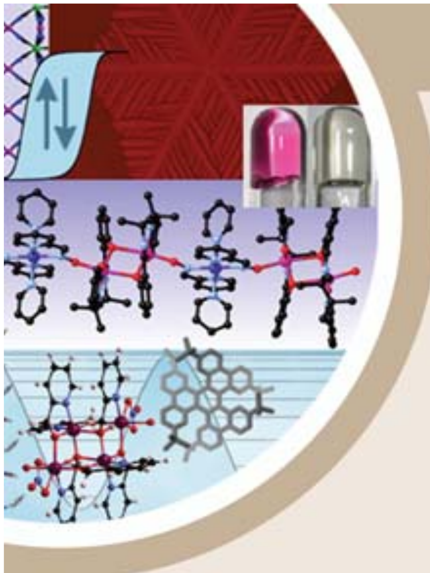
$[Mn_2(saltmen)_2Ni(pao)_2(L)_2](ClO_4)_2$







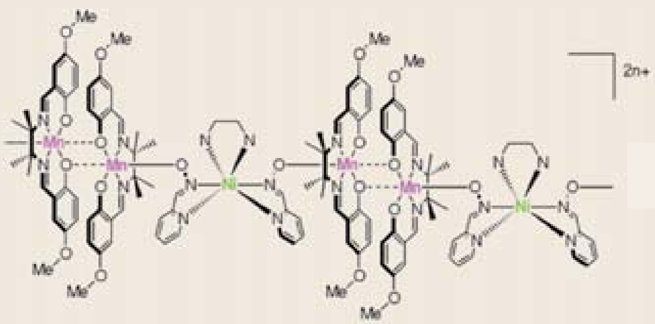
***J. Am. Chem. Soc.* 2002**, *124*, 43, 12837; ***Inorg. Chem.* 2003**, *42*, 8203

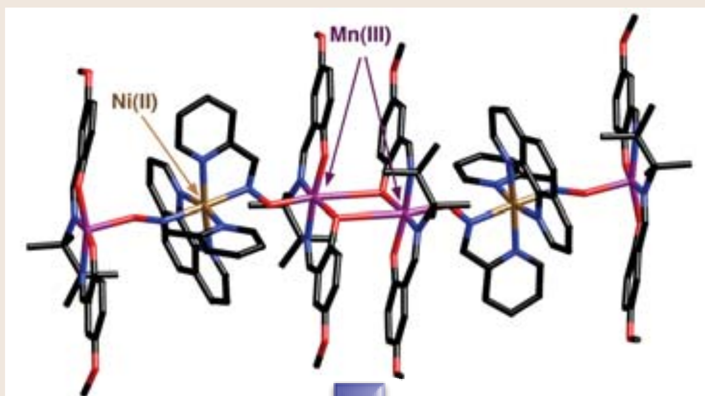


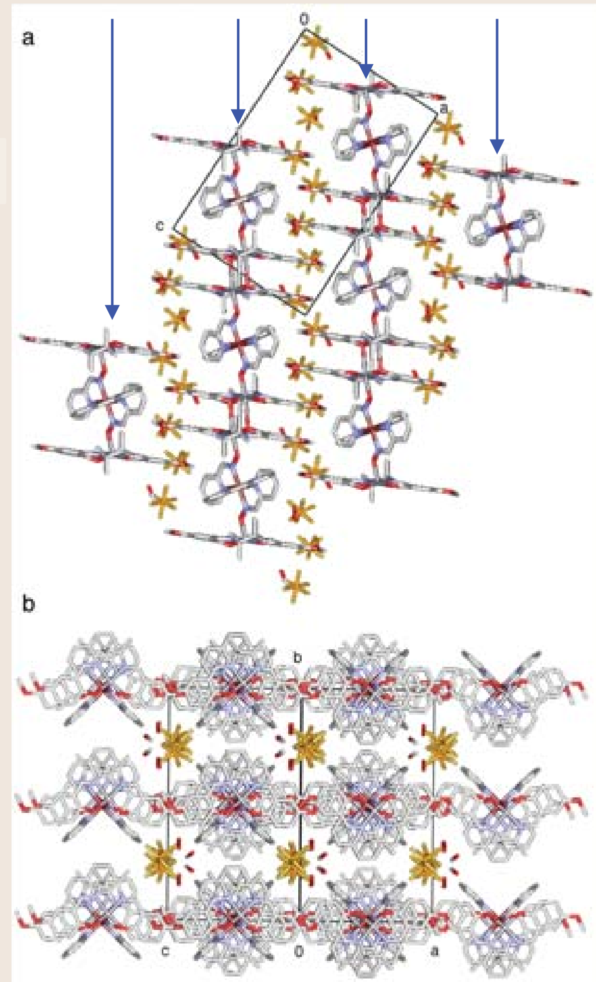
Single-Chain Magnets

Phys. Rev. Lett. **2009** *102*, 167204

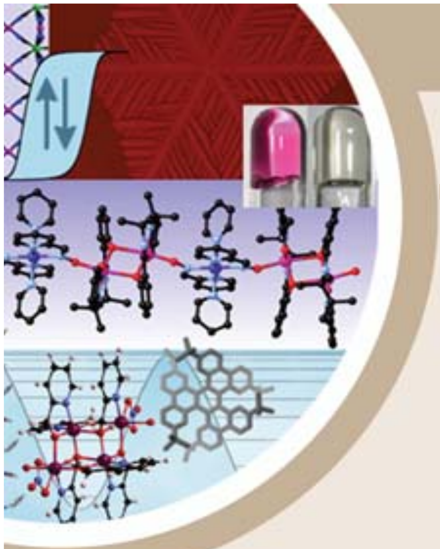
[Mn_2(5-MeOsaltmen)$_2$Ni(pao)$_2$(phen)$_2$](ClO_4)$_2$





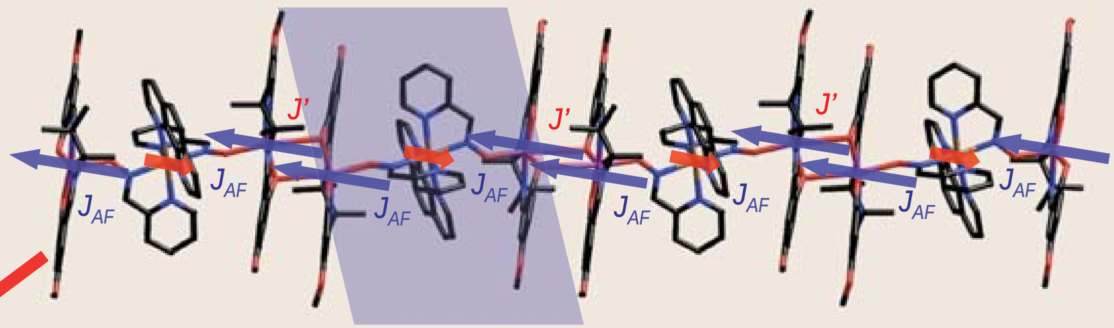


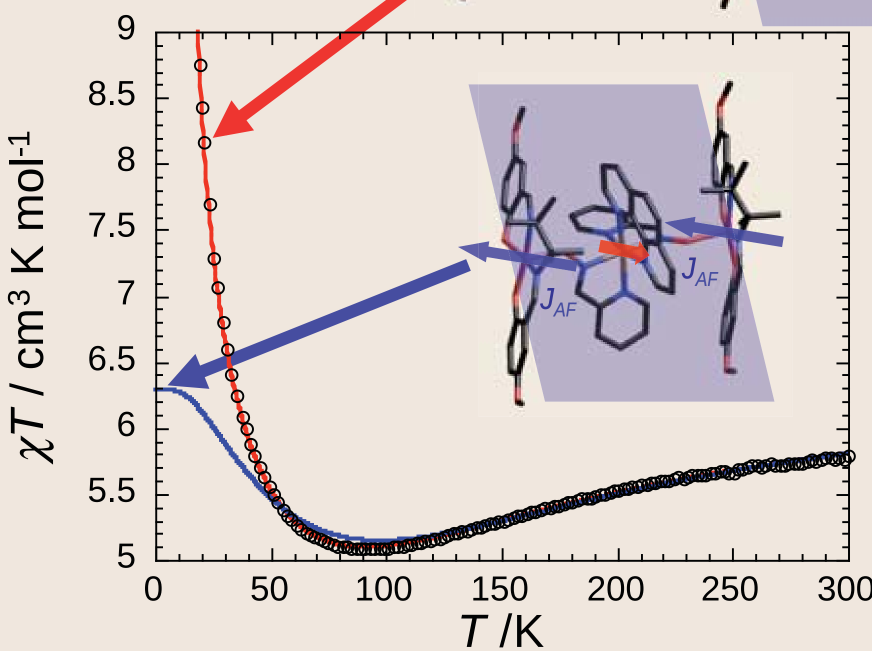
Marked changes in the chain packing induced by the 5-MeO groups…



Single-Chain Magnets

$[Mn_2(5\text{-}MeOsaltmen)_2Ni(pao)_2(phen)_2](ClO_4)_2$





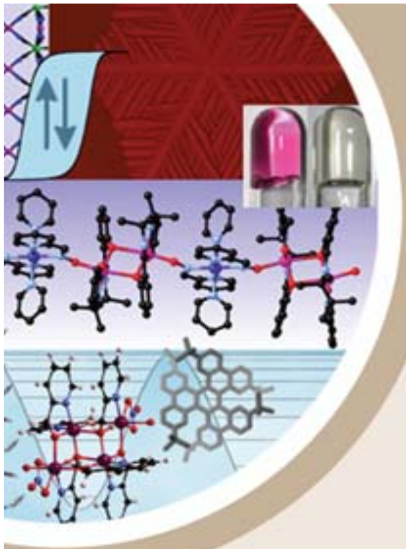
with $H = -2J_{AF}\left(\vec{S}_{Ni}\vec{S}_{Mn1} + \vec{S}_{Ni}\vec{S}_{Mn2}\right)$

An Heisenberg trimer model with inter-trimer *J'* interactions treated in a mean field approximation

$$J_{AF}/k_B = -21.9(1)\ K$$

$$J'/k_B = +0.46(5)\ K$$

$$g = 1.95(2)$$



Single-Chain Magnets

A physicist view:

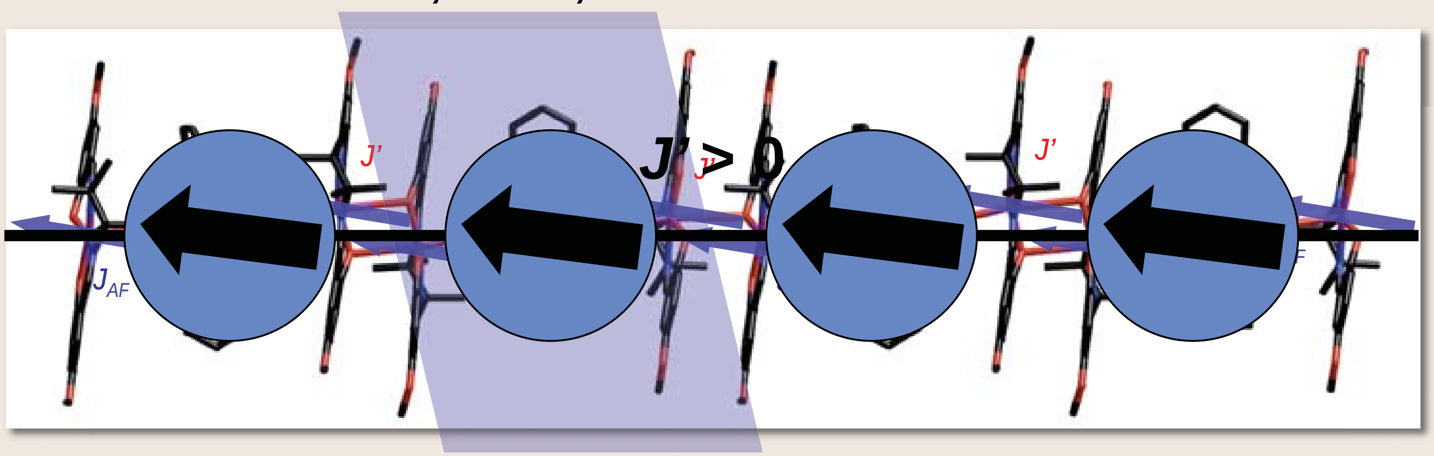
$[Mn_2(5\text{-}MeOsaltmen)_2Ni(pao)_2(phen)_2](ClO_4)_2$

J_{AF}/k_B = -21.9(1) K and J'/k_B = +0.46(5) K

« $S_T = 3$ »

S = 2, S = 1, S = 2

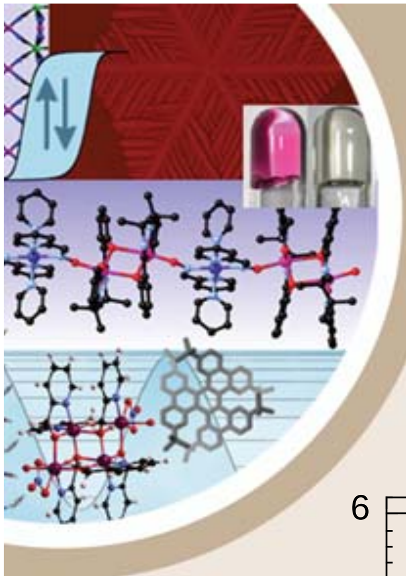
because $|J_{AF}| >> J'$ and for $|J_{AF}| >> k_B T$



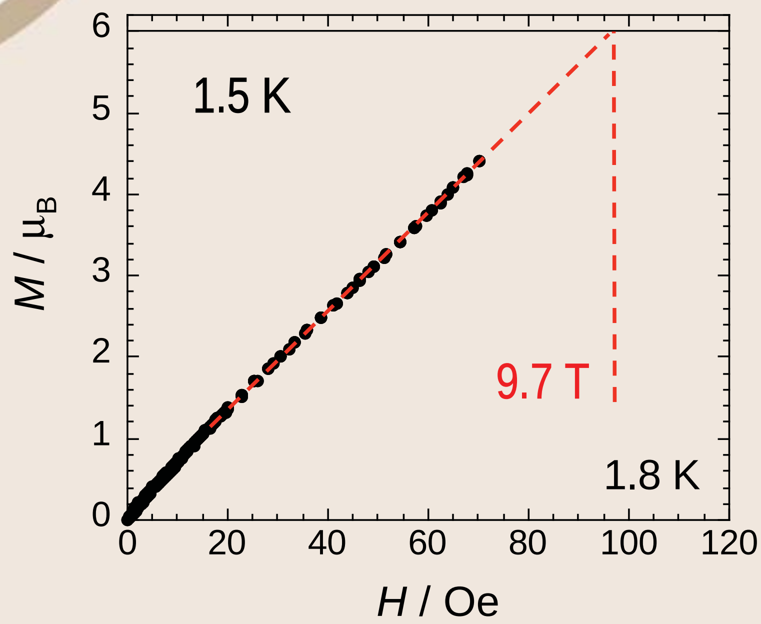
Chain of ferromagnetically coupled *S* = 3 spins

Single-Chain Magnets

Single Crystal Measurements:
***H* applied in the hard magnetic plane**



$[Mn_2(5\text{-}MeOsaltmen)_2Ni(pao)_2(phen)_2](ClO_4)_2$



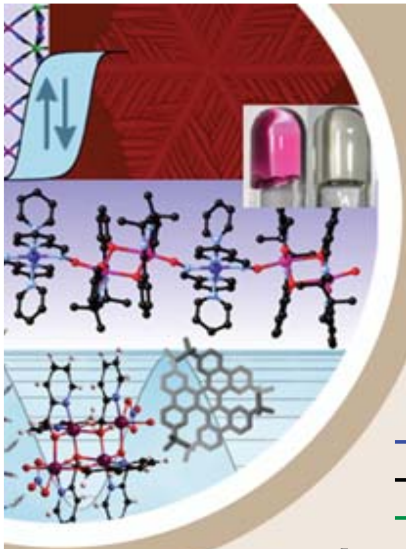
$$H = -2J'\sum_{-\infty}^{+\infty}\vec{S}_{T,i}\vec{S}_{T,i+1} + D\sum_{-\infty}^{+\infty}\vec{S}_{T,iz}^{2}$$

Estimation of *D*

$$2DS_T^2 \approx g\mu_B S_T H_a$$

D/k_B = -2.2 K

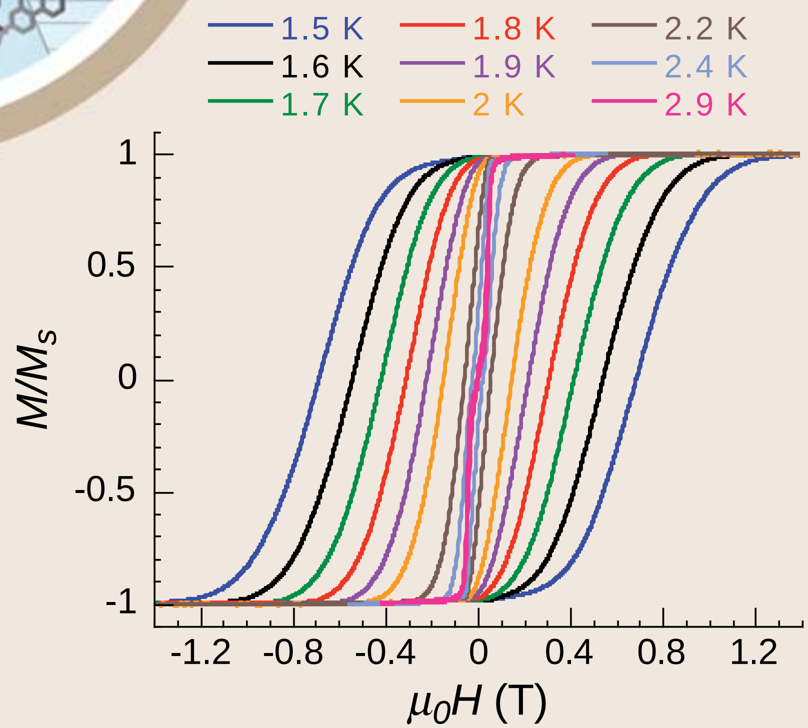
Ising type anisotropy (easy axis and hard plane)



Single-Chain Magnets

Single Crystal Measurements: *H* applied along the easy magnetic axis

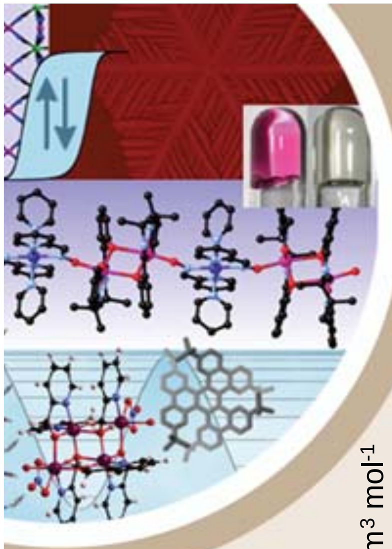
$[Mn_2(5\text{-}MeOsaltmen)_2Ni(pao)_2(phen)_2](ClO_4)_2$



M vs *H*
hysteresis loops

Magnet behavior, i.e. slow relaxation of the magnetization compatible with SCM behavior

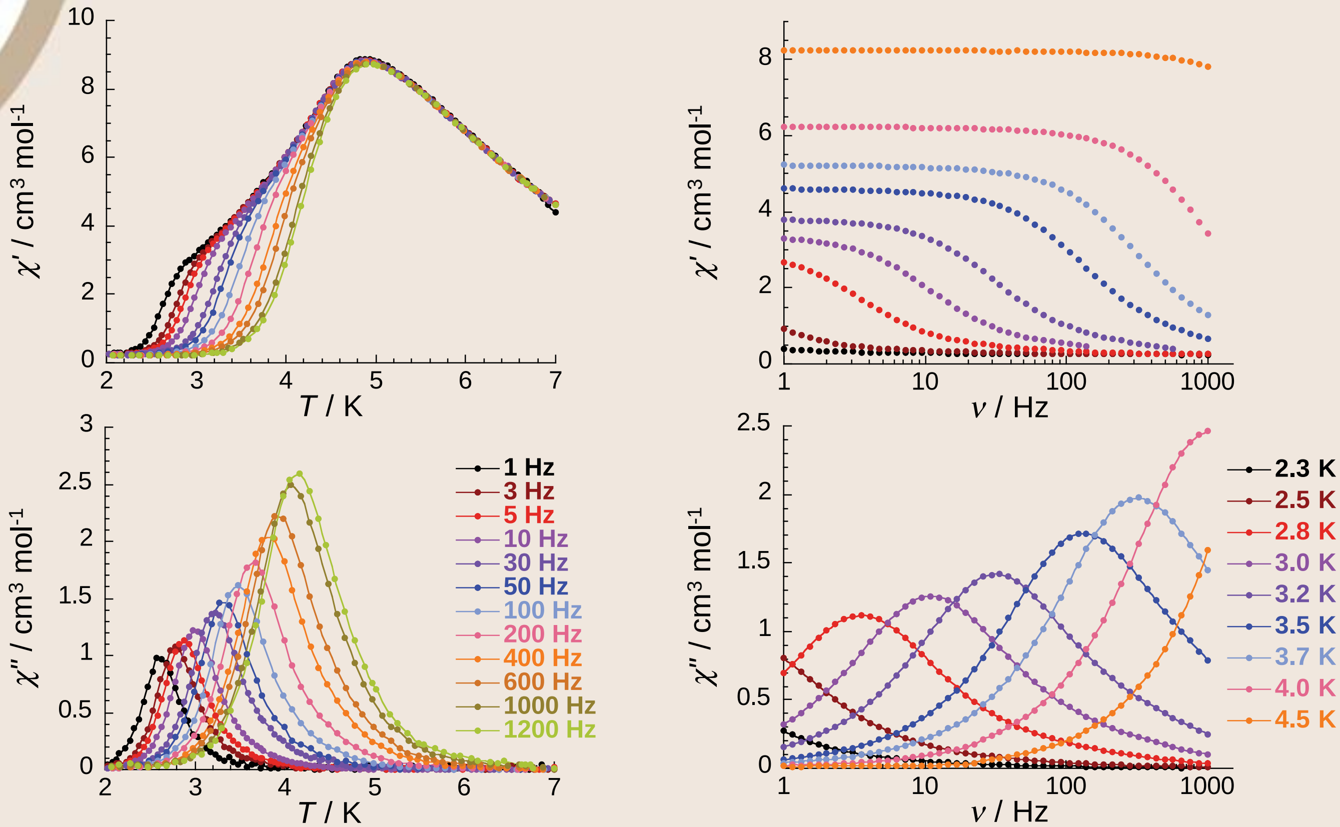
***Phys. Rev. Lett.* 2009** *102*, 167204



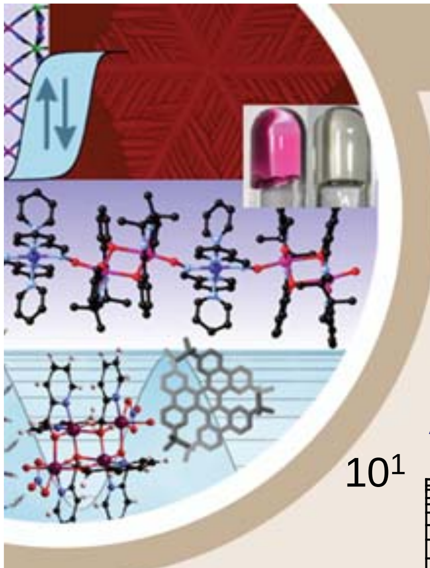
Single-Chain Magnets

Relaxation time measurements (ac susceptibility):

$[Mn_2(5\text{-}MeOsaltmen)_2Ni(pao)_2(phen)_2](ClO_4)_2$



A single relaxation mode compatible with SCM behavior but…

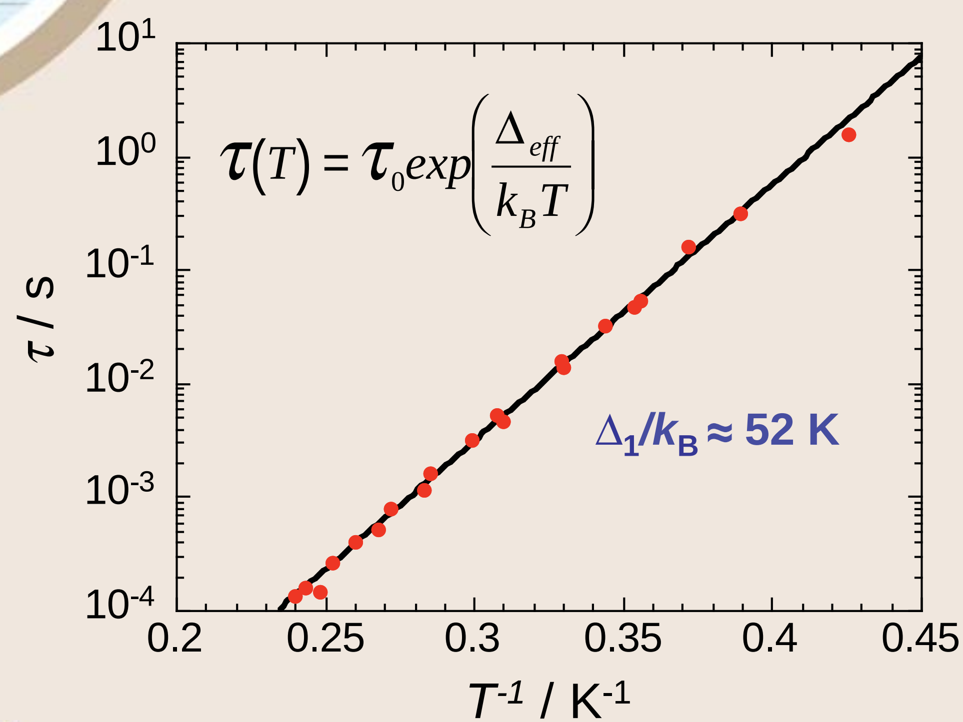


Single-Chain Magnets

Relaxation time (ac susceptibility):

$[Mn_2(5\text{-}MeOsaltmen)_2Ni(pao)_2(phen)_2](ClO_4)_2$

Arrhenius behavior



with $S_T = 3$

$J'/k_B \approx +0.46$ K

$D/k_B = -2.2$ K

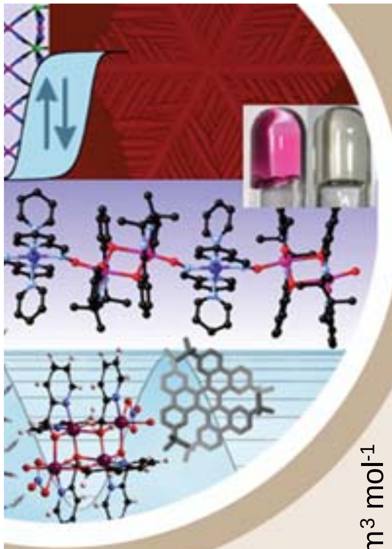
$$\tau(T) = \tau_0 exp\left(\frac{2\Delta_\xi + \Delta_A}{k_B T}\right)$$

with

$$2\Delta_\xi + \Delta_A = 8J'S_T^2 + |D|S_T^2$$

$\Delta_1/k_B = (8J' + |D|)S_T^2/k_B$
$= 52.9$ K

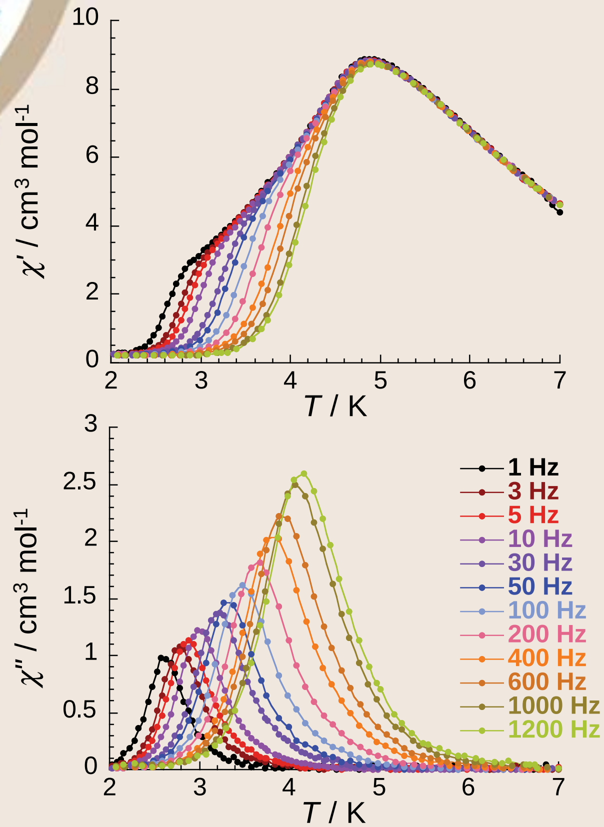
A dynamics of the magnetization compatible with a SCM…



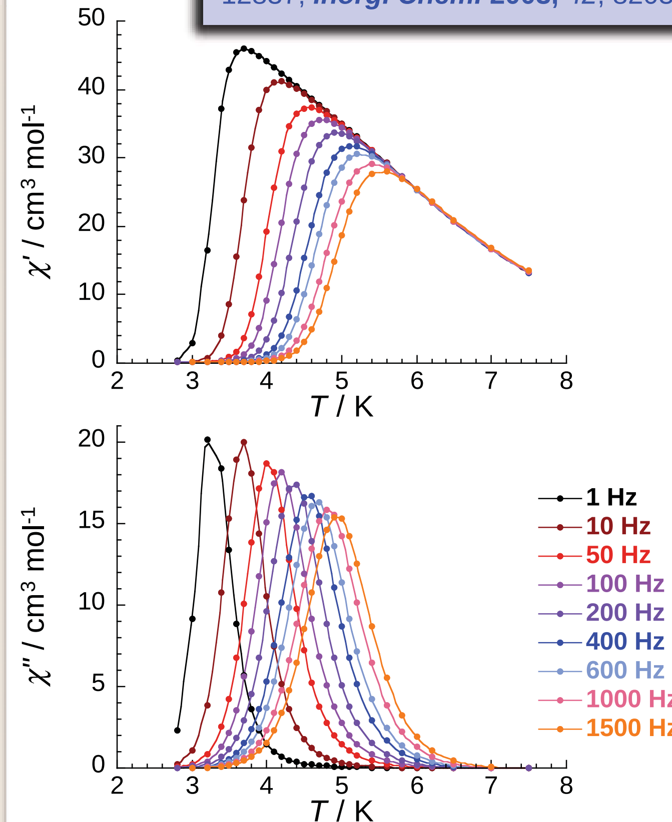
Single-Chain Magnets

Relaxation time measurements (ac susceptibility):

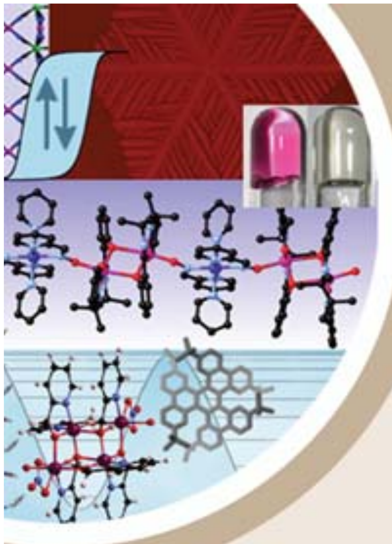
J. Am. Chem. Soc. **2002**, *124*, 12837; *Inorg. Chem.* **2003**, *42*, 8203



$[Mn_2(5\text{-}MeOsaltmen)_2Ni(pao)_2(phen)_2](ClO_4)_2$

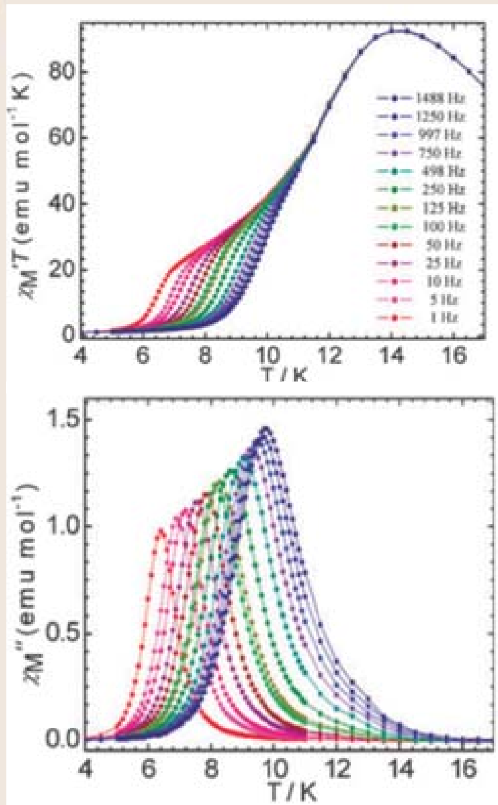


$[Mn_2(saltmen)_2Ni(pao)_2(py)_2](ClO_4)_2$



Single-Chain Magnets

Two selected examples of “SCM” systems:



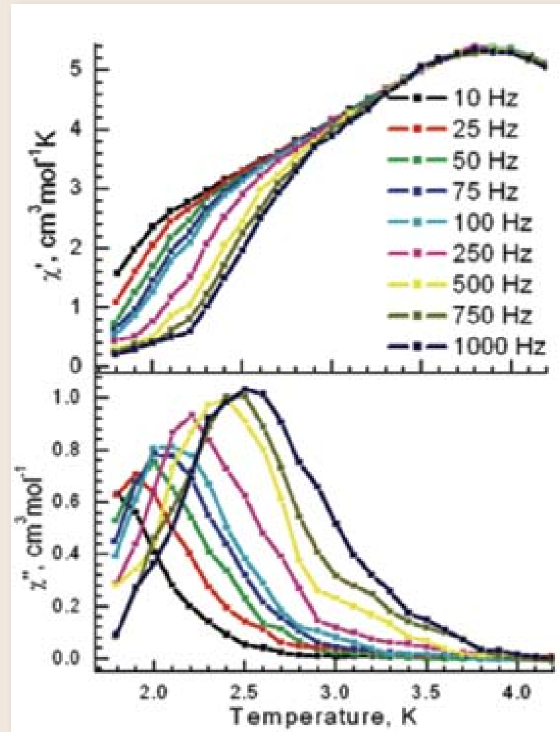


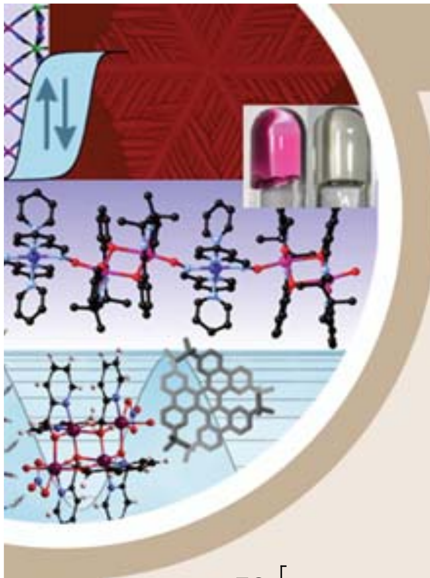
Photo-induced « SCM »…

$[Mn_6O_2(4\text{-}MeOsalox)_6(N_3)_2(MeOH)_4]$

$\{[Fe(bpy)(CN)_4]_2Co(4,4'\text{-bipyridine})\}\bullet 4H_2O$

C.-I. Yang et al. ***Chem. Commun.*** **2010,** *46*, 5716

T. Liu et al. ***J. Am. Chem. Soc.*** **2010,** *132*, 8250



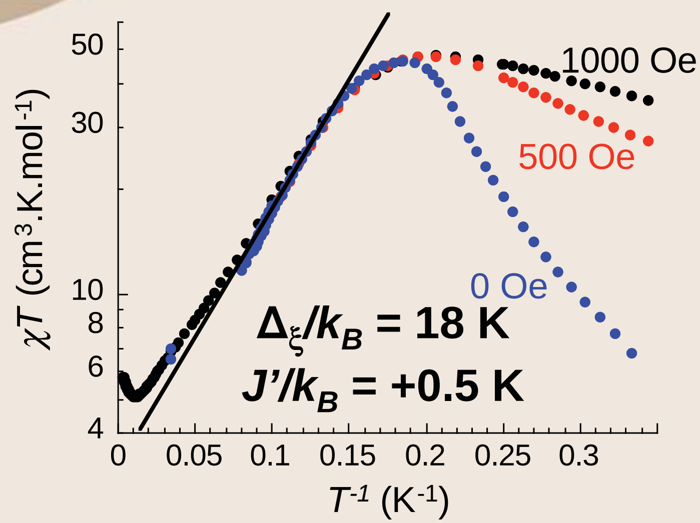
Single-Chain Magnets

One-dimensional correlation length:

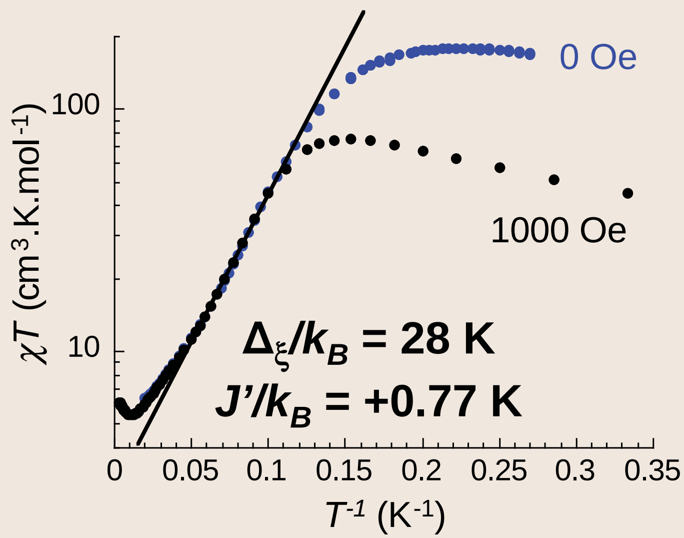
Ising Chain Model $H = -2J' S_T^2 \sum_{-\infty}^{+\infty} \vec{\sigma}_i \vec{\sigma}_{i+1}$

$$\chi = \frac{C_{eff}}{T} exp\left(\frac{\Delta_\xi}{k_B T}\right) \quad \text{with } \Delta_\xi = 4J' S_T^2$$

Infinite chain regime $\xi < L$

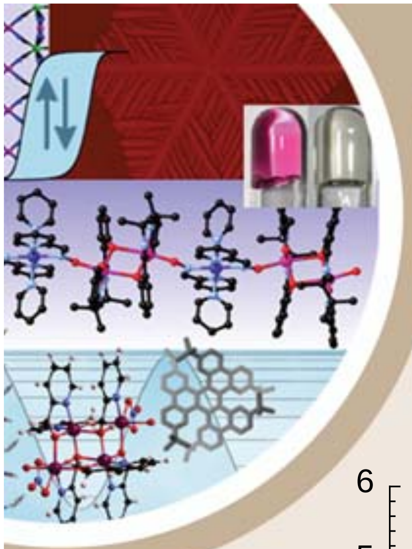


$[Mn_2(5\text{-}MeOsaltmen)_2Ni(pao)_2(phen)_2](ClO_4)_2$



$[Mn_2(saltmen)_2Ni(pao)_2(py)_2](ClO_4)_2$

One dimensional properties: Single-Chain Magnet, but…

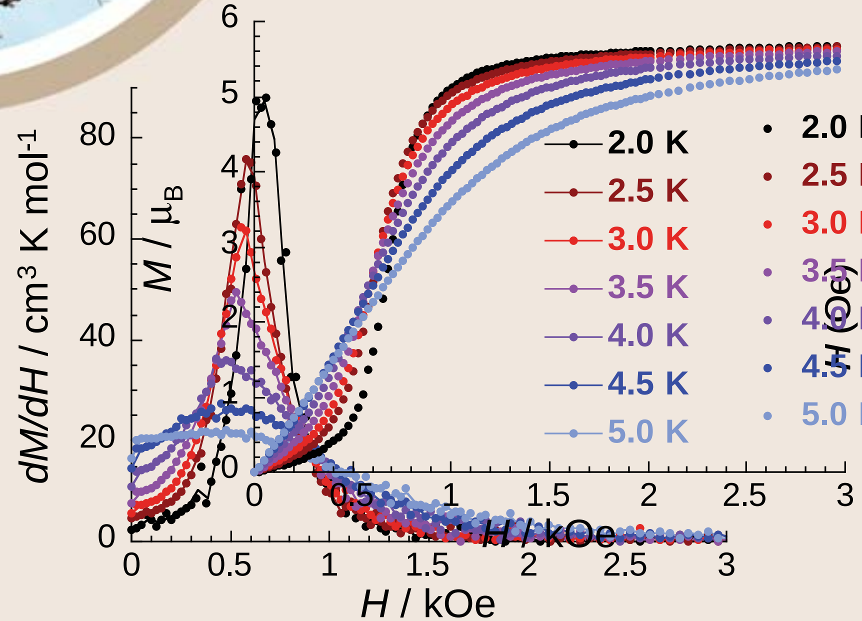


A Single-Chain Magnet behavior or not?

Field dependence of the magnetization:

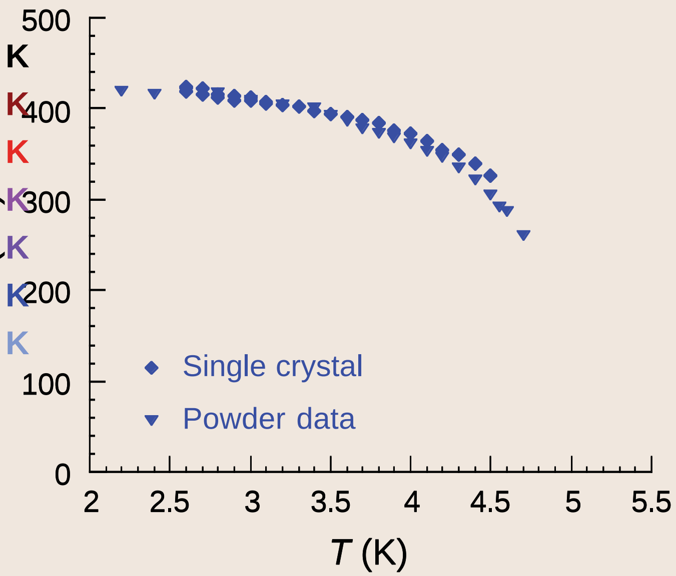
$[Mn_2(5\text{-}MeOsaltmen)_2Ni(pao)_2(phen)_2](ClO_4)_2$

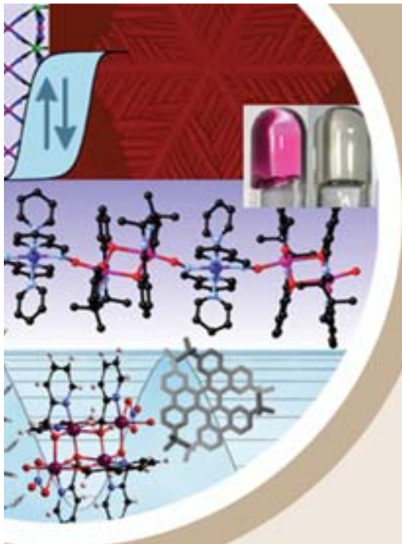
***Phys. Rev. Lett.* 2009** *102*, 167204



Single crystal (easy axis)

(*T, H*) Phase diagram



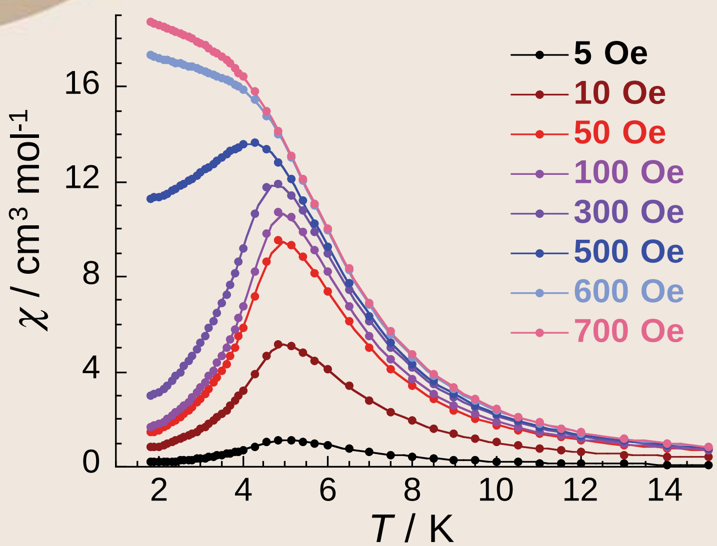


A Single-Chain Magnet behavior or not?

Temperature dependence of the susceptibility:

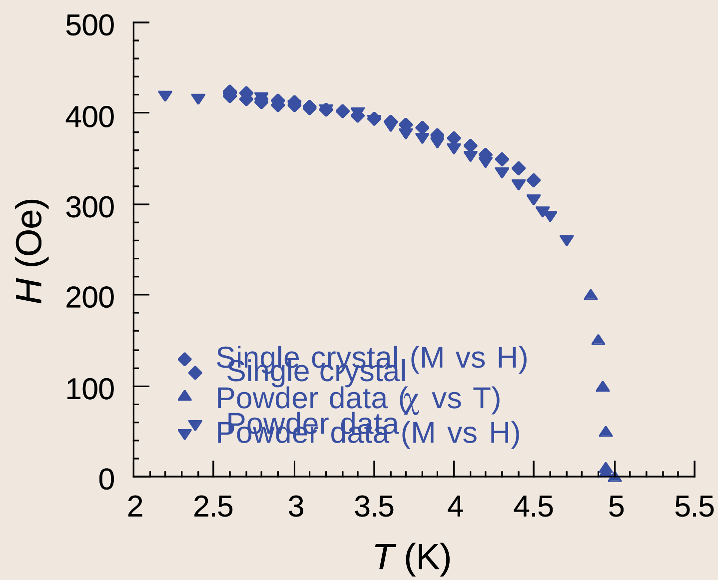
$[Mn_2(5\text{-}MeOsaltmen)_2Ni(pao)_2(phen)_2](ClO_4)_2$

***Phys. Rev. Lett.* 2009** *102*, 167204



Powder measurements

(*H*, *T*) Phase diagram

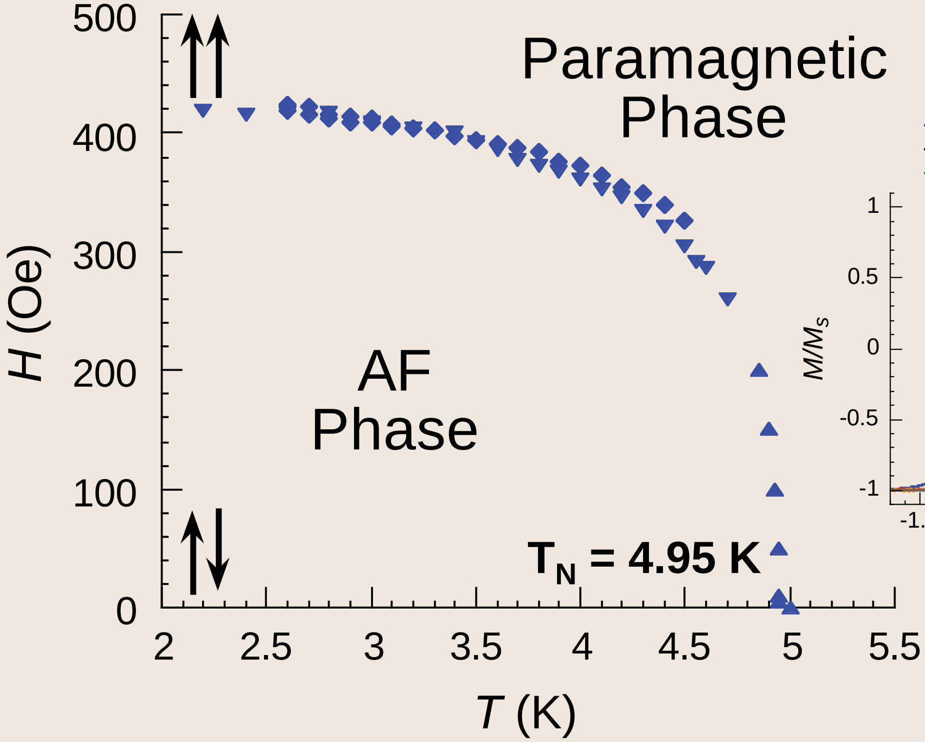


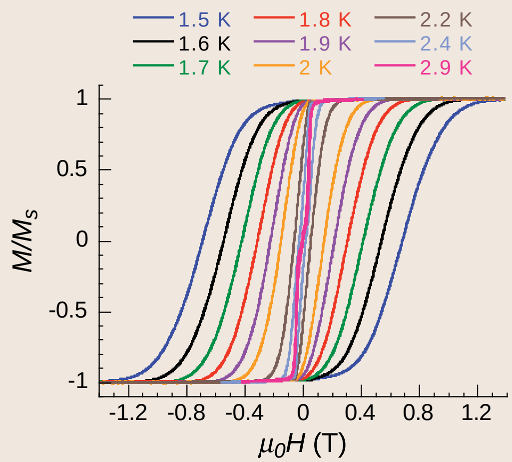
A Single-Chain Magnet behavior or not?

Metamagnetic behavior:

$[Mn_2(5\text{-}MeOsaltmen)_2Ni(pao)_2(phen)_2](ClO_4)_2$

(H, T) Phase diagram



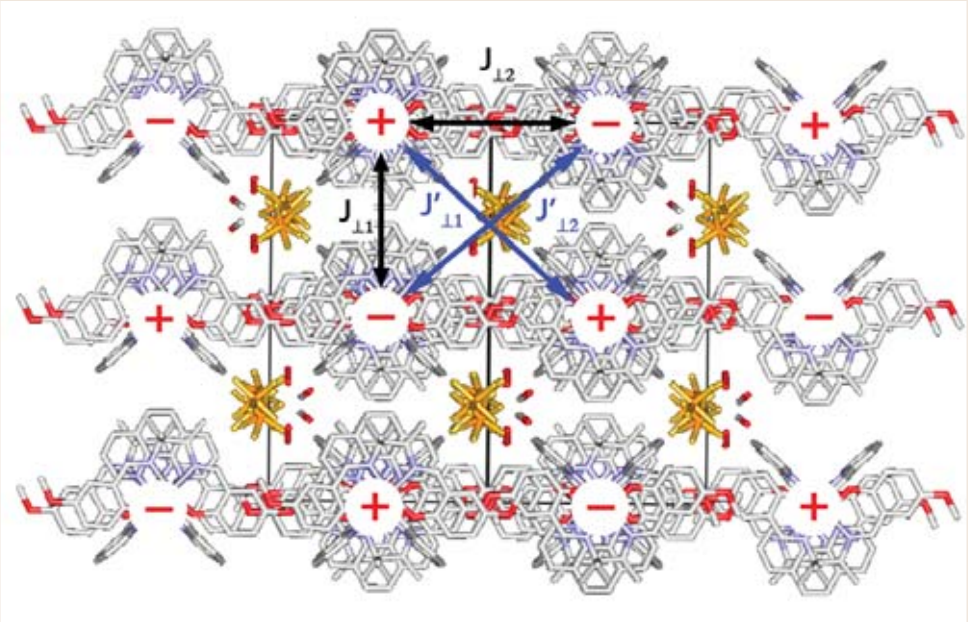


An antiferromagnetic phase… BUT also a MAGNET !!!

A Single-Chain Magnet behavior or not?

Two-sublattices model in the Ising limit treating the interchain interactions in the mean field approximation:

A possible magnetic structure:

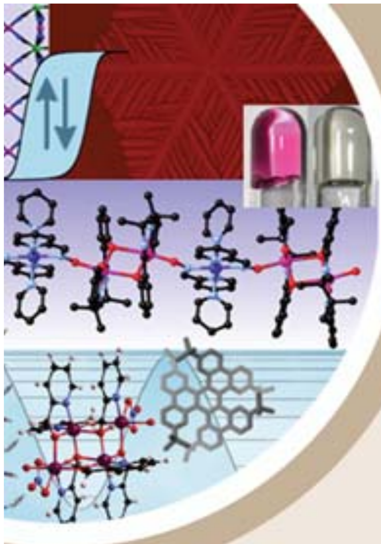


$$J_{\perp} = \frac{(J_{\perp 1} + J_{\perp 2})}{2}$$

$$J'_{\perp} = \frac{(J'_{\perp 1} + J'_{\perp 2})}{2}$$

$$\text{with } |J'_{\perp i}| < |J_{\perp i}|$$

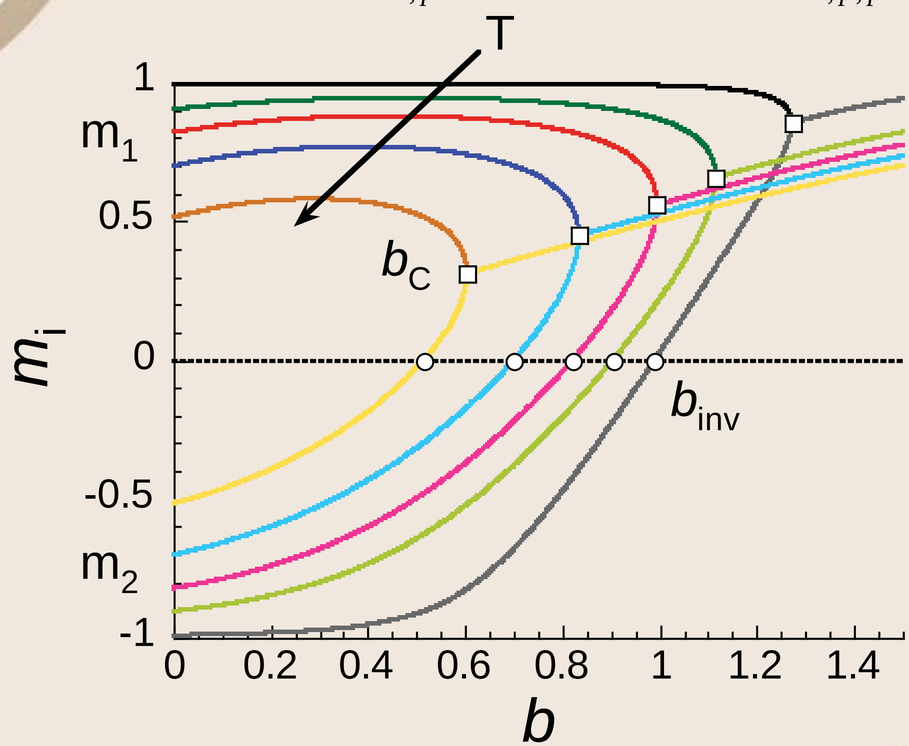
Phys. Rev. Lett. **2009** *102*, 167204



A Single-Chain Magnet behavior or not?

Two-sublattices model in the Ising limit treating the interchain interactions in the mean field approximation:

$$H = -2J_{//}S_T^2\sum_{n,p}\sigma_{n+1,p}\sigma_{n,p} - 2J_{\perp}S_T^2\sum_{n,p,p'}\sigma_{n,p}\sigma_{n,p'}$$

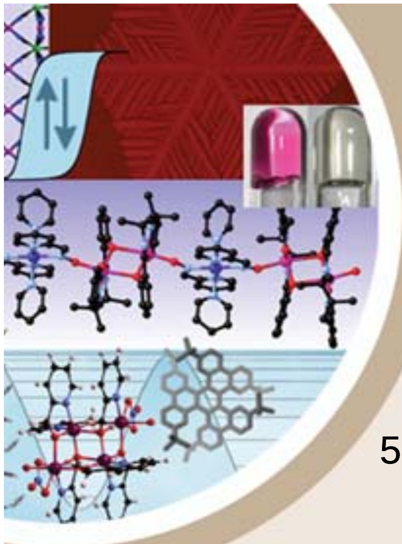


$$J_{\|}/k_B = J'/k_B = +0.5\ \mathrm{K}$$

$$r = \frac{z'J'_{\perp}}{zJ_{\perp}} = 0.3$$

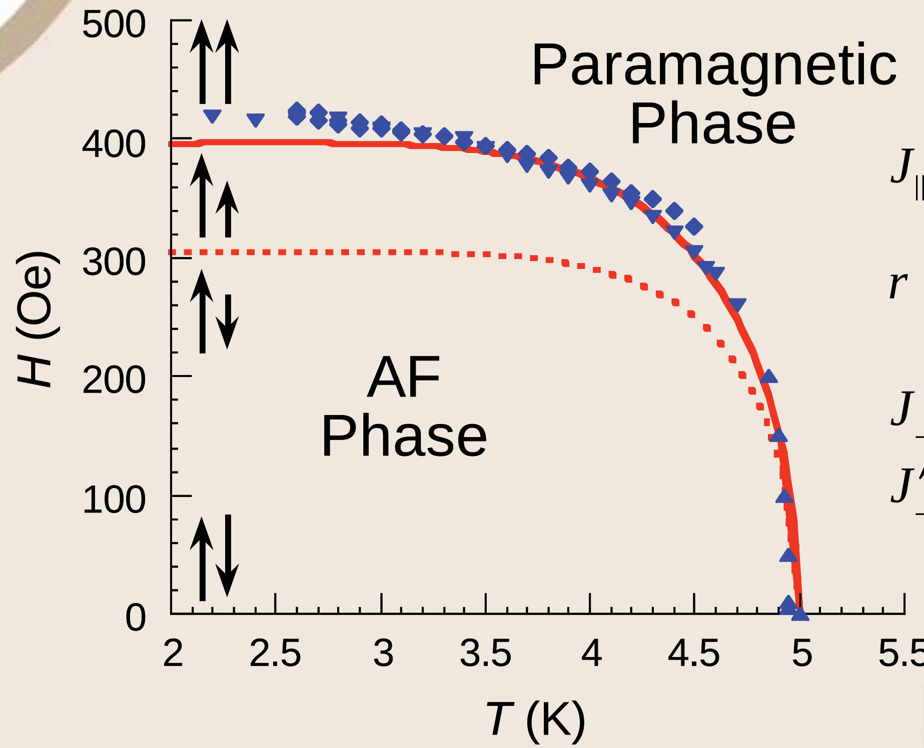
$$b = -\frac{\mu_B H}{2zJ_{\perp}S_T}$$

Phys. Rev. Lett. **2009** *102*, 167204



A Single-Chain Magnet behavior or not?

Two-sublattices model in the Ising limit treating the interchain magnetic interactions in the mean field approximation:



$$J_{\parallel}/k_B = J'/k_B = +0.5\ \mathrm{K}$$

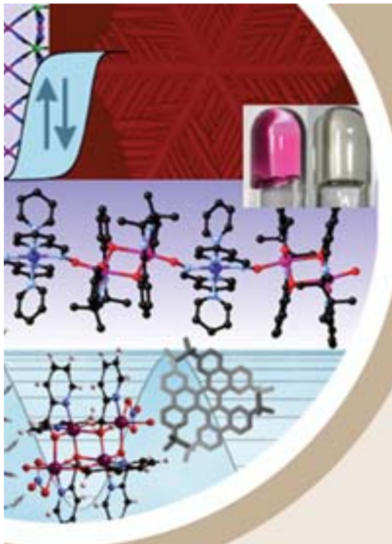
$$r = \frac{z'J'_{\perp}}{zJ_{\perp}} = 0.3$$

$$J_{\perp}/k_B \approx -0.005\ \mathrm{K}$$

$$J'_{\perp}/k_B \approx -0.0015\ \mathrm{K}$$

***Phys. Rev. Lett.* 2009** *102*, 167204

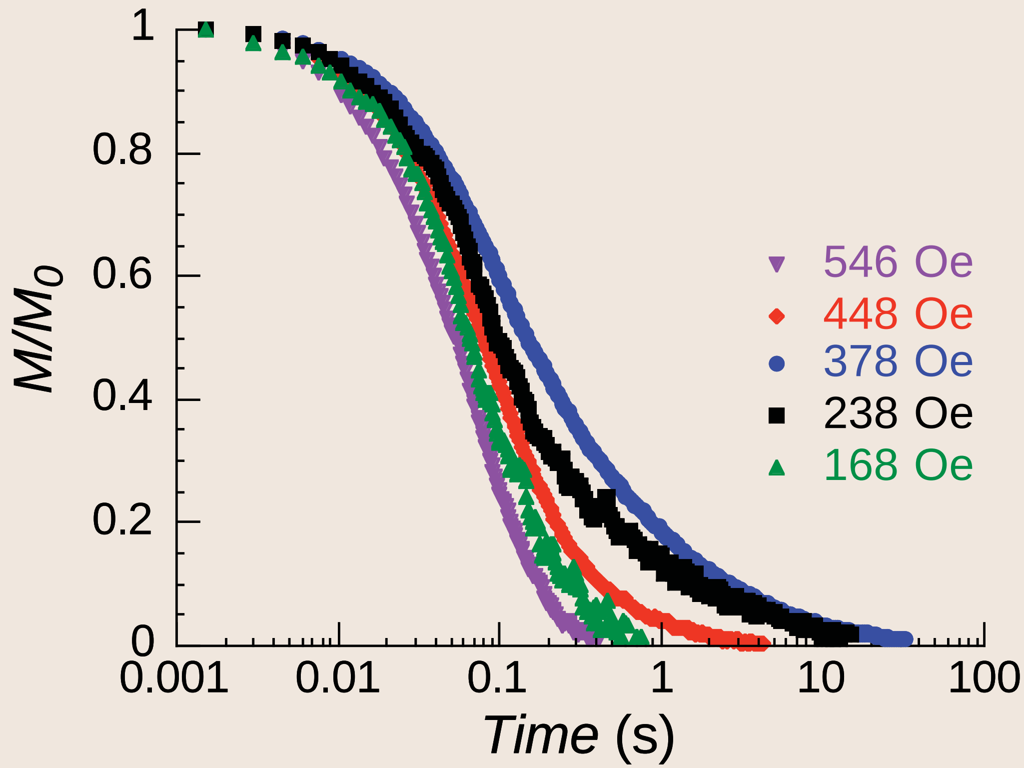
An antiferromagnetic phase of Chains



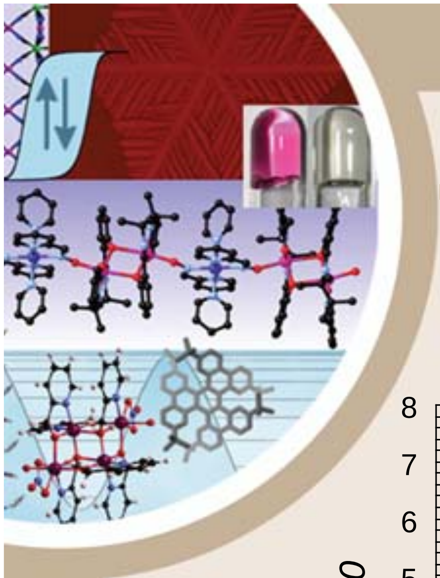
A Single-Chain Magnet behavior or not?

Dynamics of the magnetization under applied dc field:

T = 2.9 K

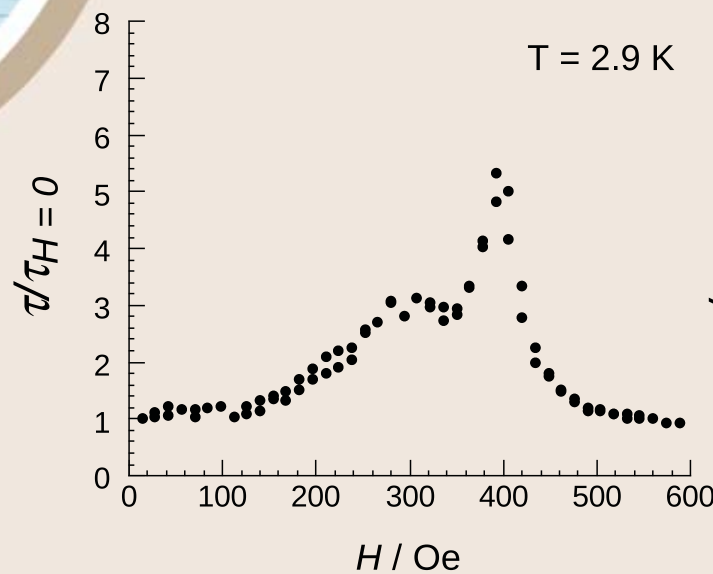


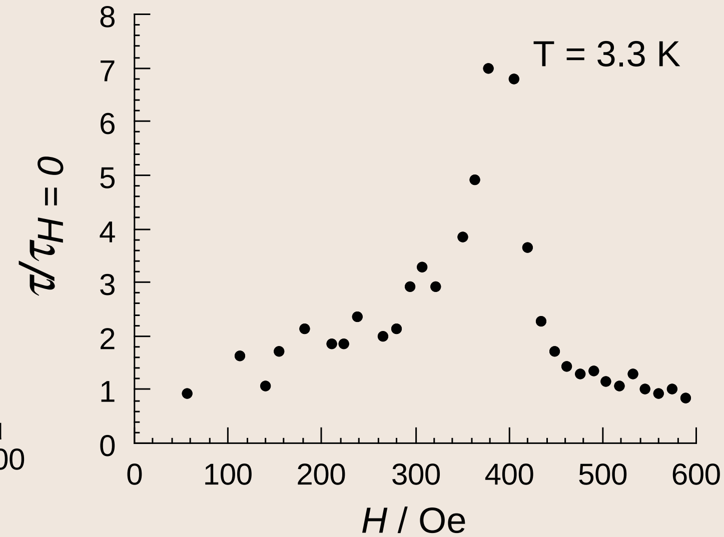
***Phys. Rev. Lett.* 2009** *102*, 167204



A Single-Chain Magnet behavior or not?

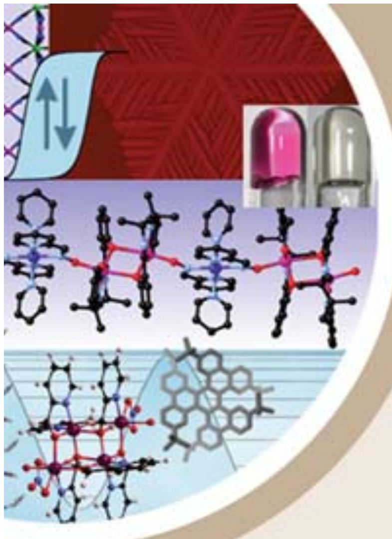
Dynamics of the magnetization under applied dc field:





A maximum of the relaxation time is found at the critical field… maybe a second extremum…

Phys. Rev. Lett. **2009** *102*, 167204



A Single-Chain Magnet behavior or not?

Dynamics of the magnetization under applied dc field:

Linear response with the inter-chain interactions treated in the mean field approximation:

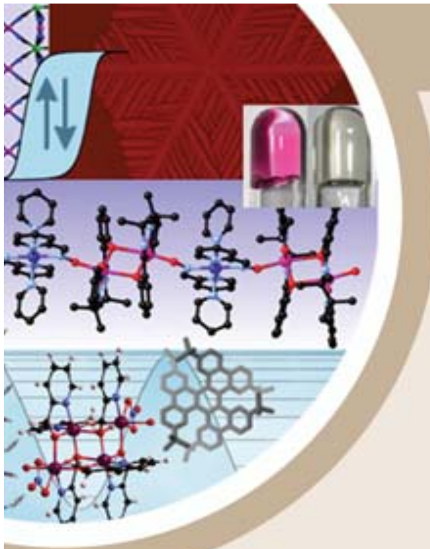
$$\frac{1}{\tau}=\frac{1}{2}\left(\frac{1-A_1'}{\tau_1}+\frac{1-A_2'}{\tau_2}\right)-\frac{1}{2}\sqrt{\left(\frac{1-A_1'}{\tau_1}-\frac{1-A_2'}{\tau_2}\right)^2+4\frac{A_1A_2}{\tau_1\tau_2}}$$

τ_i are the relaxation times of the isolated chain in their effective magnetic field

***Phys. Rev. Lett.* 2009** *102*, 167204

$$A_i=-(1-m_i^2)^{3/2}\frac{4z\left|J_\perp\right|S_T^2}{k_BT\exp(-4J_{//}S_T^2/k_BT)}$$

$$A_i'=-(1-m_i^2)^{3/2}\frac{4z'\left|J_\perp'\right|S_T^2}{k_BT\exp(-4J_{//}S_T^2/k_BT)}$$

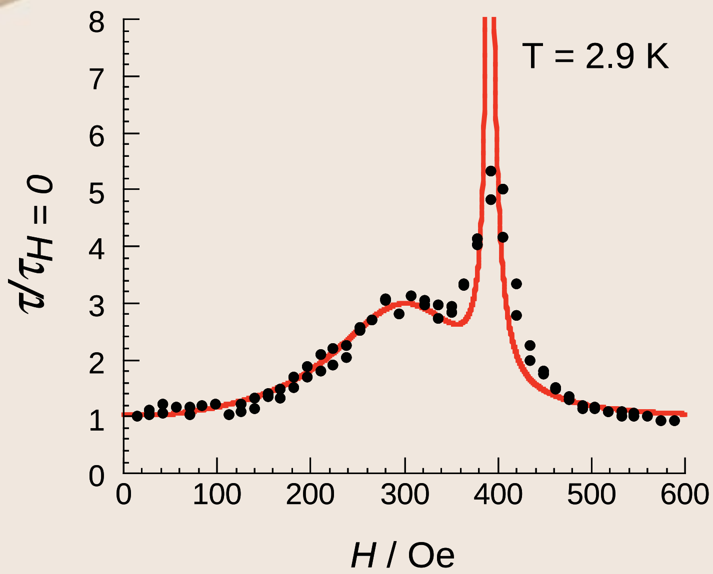


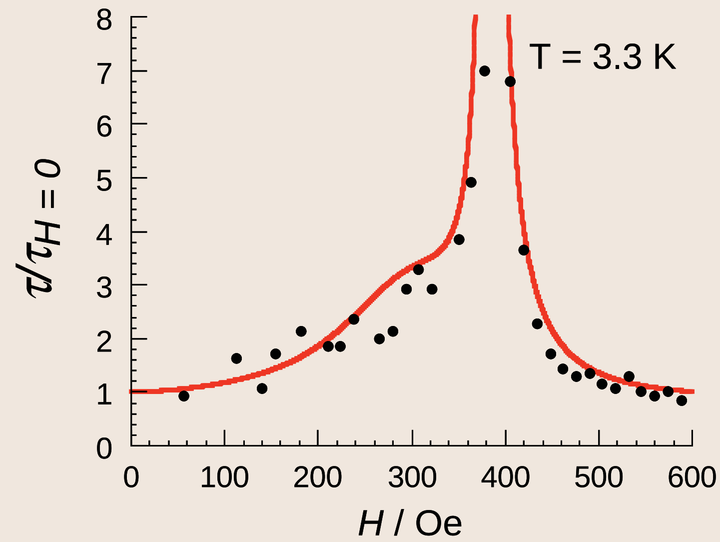
A Single-Chain Magnet behavior or not?

Dynamics of the magnetization under applied dc field:

Linear response with the inter-chain interactions treated in the mean field approximation:

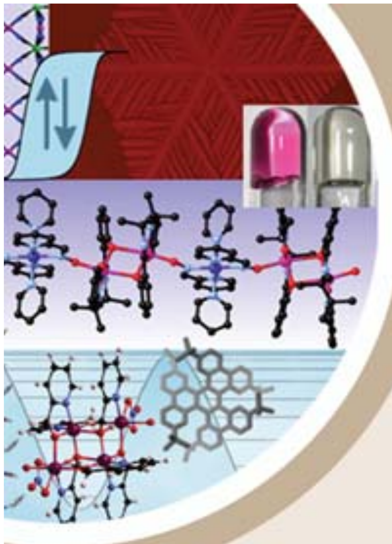
$$\frac{1}{\tau}=\frac{1}{2}\left(\frac{1-A_1'}{\tau_1}+\frac{1-A_2'}{\tau_2}\right)-\frac{1}{2}\sqrt{\left(\frac{1-A_1'}{\tau_1}-\frac{1-A_2'}{\tau_2}\right)^2+4\frac{A_1A_2}{\tau_1\tau_2}}$$





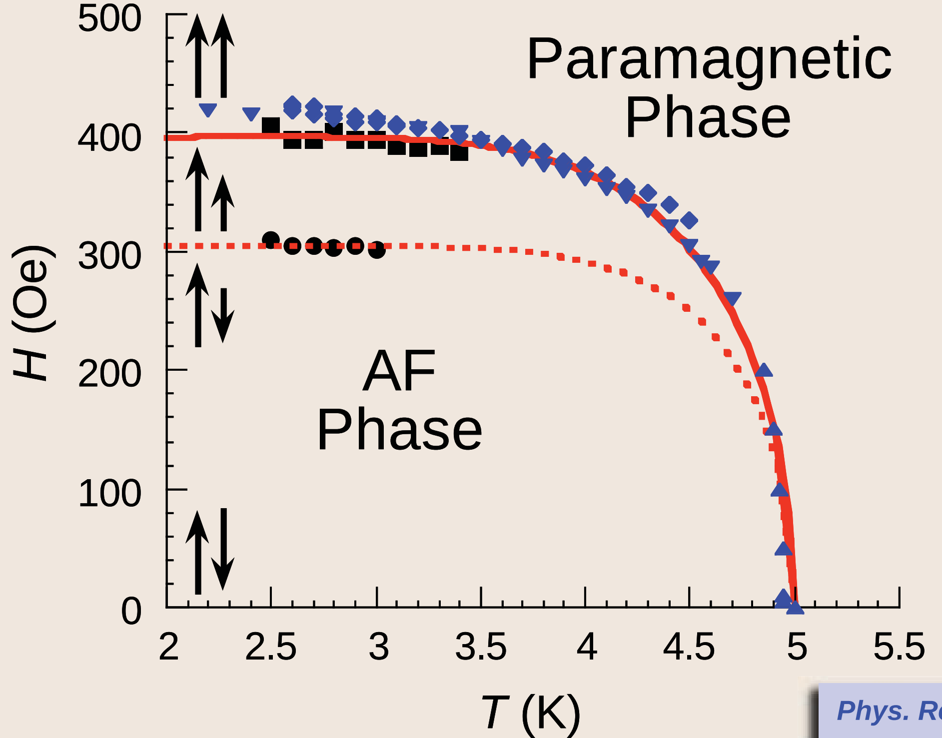
$T_N = 5\ \mathrm{K}$ $\quad r=\frac{z'J_\perp'}{zJ_\perp}=0.3$ $\quad J_\parallel/k_B=+0.5\ \mathrm{K}$

Phys. Rev. Lett. **2009** *102*, 167204



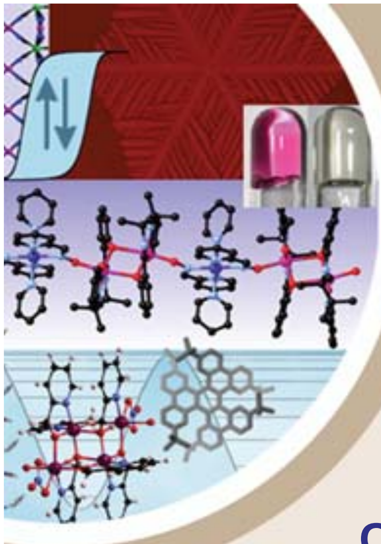
A Single-Chain Magnet behavior or not?

Two-sublattices model in the Ising limit treating the interchain magnetic interactions in the mean field approximation: A perfect agreement between static and dynamic properties



Phys. Rev. Lett. **2009** *102*, 167204

An antiferromagnetic ordered phase of Single-Chain Magnets



A Single-Chain Magnet behavior or not?

Strictly speaking: NO

***Phys. Rev. Lett.* 2009** *102*, 167204;
***Chem. Eur. J.* 2010** *16*, 3656

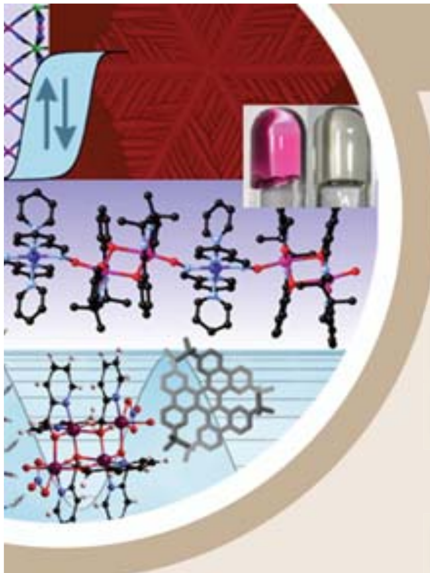
An 3D antiferromagnetic ordered phase of Single-Chain Magnets…

Completely described (static and dynamics properties) by a simple two-sublattices Ising model with the interchain magnetic interactions treated in the mean field approximation

- **The existence of an AF order does not prevent slow dynamics of the magnetization induced by the presence of Single-Chain Magnet**

- **Slowing down of the relaxation is even observed close to the AF-Paramagnetic transition line.**

- **Introduction of large intrachain interactions between anisotropic spins could promote high-blocking SCM-based materials independently of the presence of an ordered AF phase.**



Acknowledgements:

The « Molecular Magnetic Material » team:

- C. Coulon (Prof.)
- P. Dechambenoit (A. Prof.)
- E. Hillard (CNRS Res.)
- M. Rouzières (A. Eng.)

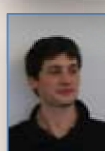


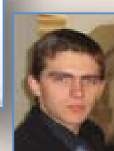

Postdocs:

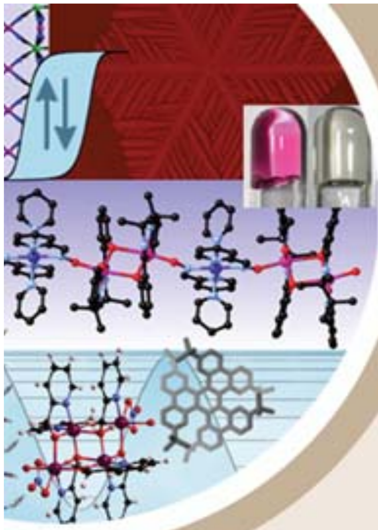
Dr. Céline Pichon, Dr. Dalice Pinero

Ph-D Students:

- 3rd year:
  Ie-Rang Jeon
  Indrani Bhowmick
- 2nd year:
  Dmitri Mitcov
- 1st year:
  Vivien Pianet, Mihail Secu,
  Kasper Steen Pedersen





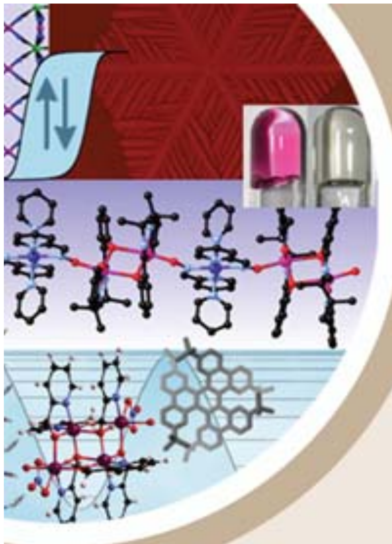
Acknowledgements:

- *Kanazawa University, Japan*

  Prof. Hitoshi Miyasaka and his group

- *Institut Néel, Grenoble, France*

  Dr. Wolfgang Wernsdorfer



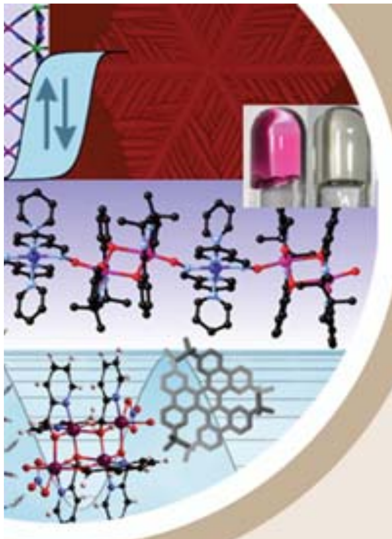
Acknowledgements:

- CNRS
- *University of Bordeaux* (UNIVERSITÉ DE BORDEAUX; UNIVERSITÉ BORDEAUX 1 Sciences Technologies)
- ANR (AGENCE NATIONALE DE LA RECHERCHE) *MAGNETCAT and AC-MAGnets*
- *Conseil régional d'Aquitaine (Magnetometer, EPR, X-ray Diffractometer, PPMS)* (REGION AQUITAINE)
- *The organizing committee*

ICMM–ORLANDO 2012

ICMM 2012

The 13th **I**nternational **C**onference on **M**olecule-based **M**agnets



The end…

Thank you for Your attention!